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**Singlet Oxygen Generators for Chemical Oxygen-Iodine Laser – A Literature Review**

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# Singlet Oxygen Generators for Chemical Oxygen-Iodine Laser - A Literature Review

## Executive Summary

There exists a significant database on the scientific knowledge and technical know-how associated with the chemical oxygen-iodine laser (COIL) as a result of extensive R&D efforts by the U.S. and international government and private organizations in the past 30 years. As one of the key COIL subsystems, the singlet oxygen generator (SOG) is critical in determining the overall chemical efficiency of the laser process. The first singlet oxygen generator based on the chlorine-basic hydrogen peroxide (BHP) reaction was reported in 1978. The goal of this literature review is to provide a chronological overview on the technology development, engineering design database, and state-of-the-art of singlet oxygen generators based on the chlorine-basic hydrogen peroxide (BHP) reaction for COIL applications. Literature sources for this review primarily consist of scientific journals, SPIE and AIAA proceedings, and U.S. Patents covering the time period from 1978 to present. Major sections in this review include: (1) introduction of singlet oxygen and relevant COIL chemistry; (2) singlet oxygen generation based on the chlorine - basic hydrogen peroxide (BHP) reaction; (3) singlet oxygen generator designs and typical characteristics; (4) prediction of SOG performance; (5) SOG improvement aspects; (6) other related issues; and (7) appendices including gas-liquid reactor design, chemical/reaction databases; and the results from a preliminary U.S. patent search. The SOG development has evolved from a rudimentary design (the chlorine-bubbler) to the rotating-disk design, and to the current state-of-the-art design - a hybrid between the jet and the aerosol SOGs. The performance of these SOGs typically falls in the range of 80% for the singlet oxygen yield and 98% for the chlorine utilization efficiency. A comparison of their unit operations shows these four types of SOGs share a common design approach. Significant improvements in the SOG performance, in terms of singlet oxygen flux and transport, chemical efficiency, and logistics requirements, are likely to be accomplished by developing a new generation of SOGs based on novel design approaches that can effectively manage the negative impacts of water from the chlorine-BHP reaction, system pressure, and heat of reactions.

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## List of Symbols

- A - pre-exponential factor determined by the geometric configuration of the diffusing solute gas in the liquid solvent and the partition functions for viscosity,
- $A_S$  - the total surface area of the jet columns ( $\text{cm}^2$ ),
- C - the concentration ( $\text{gmole/L}$  or  $\text{gmole/cm}^3$ ),
- $C_A, C_B$  - the concentration of species A and B ( $\text{gmole/L}$  or  $\text{gmole/cm}^3$ ),
- $C_A^*$  - the equilibrium concentration ( $\text{gmole/cm}^3$ ) of dissolved gas corresponding to  $p_i$ ,
- $C_{A0}$  - the average concentration ( $\text{gmole/cm}^3$ ) of dissolved gas in the bulk liquid,
- $C_{B0}$  - the average concentration ( $\text{gmole/cm}^3$ ) of reactant in the bulk liquid,
- $C_1^g$  - the concentration of  $\text{Cl}_2$  in the bulk gas phase ( $\text{mol/cm}^3$ ),
- $C_3^g$  - the concentration of  $\text{O}_2(^1\Delta_g)$  in the bulk gas phase ( $\text{mol/cm}^3$ ),
- $C_2$  - the concentration of  $\text{HO}_2^-$  at the liquid surface ( $\text{mol/cm}^3$ ),
- D - the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),
- $D_A$  - the molecular diffusivity of dissolved gas A in very dilution solution ( $\text{cm}^2/\text{s}$ ),
- $D_B$  - the molecular diffusivity of liquid B in very dilution solution ( $\text{cm}^2/\text{s}$ ),
- $D_{AB}$  - the diffusivity of species A in species B ( $\text{cm}^2/\text{s}$ ),
- $D_{\text{Cl}_2\text{-BHP}} (D_1)$  - the diffusion coefficient of  $\text{Cl}_2$  in BHP ( $\text{cm}^2/\text{s}$ ),
- $D_2$  - the diffusion coefficient of  $\text{HO}_2^-$  in BHP ( $\text{cm}^2/\text{s}$ ),
- $D_{\text{O}_2\text{-BHP}} (D_3)$  - the diffusion coefficient of  $\text{O}_2(^1\Delta_g)$  in BHP ( $\text{cm}^2/\text{s}$ ),
- $D_1^g$  - the diffusion coefficient of  $\text{Cl}_2$  in the gas phase or gas phase diffusivity ( $\text{cm}^2/\text{s}$ ),
- $D_3^g$  - the diffusion coefficient of  $\text{O}_2(^1\Delta_g)$  in the gas phase ( $\text{cm}^2/\text{s}$ ),
- $D_h$  - the hydraulic diameter or characteristic length (cm),
- E - the enhancement factor (dimensionless),
- $E_d$  - the activation energy for diffusion,
- H - Henry's law constant ( $\text{atm cm}^3/\text{gmole}$ ,  $\text{atm L/gmole}$ , or  $\text{kPa cm}^3/\text{gmole}$ ),
- Ha - Hatta number  $(D_A k_2 C_{B0})^{1/2}/k_L$  (dimensionless),
- $\Delta H_{\text{RX}}$  - the heat of reaction ( $\text{kcal/gmole}$  or  $\text{kJ/gmole}$ ),
- L - the length of diffusion path (cm),
- M - the chemical magnification ( $= C_2^0/C_1^{g0}$ ),
- $N_A$  - the flux of species A ( $\text{gmole/cm}^2 \text{ s}$ ),
- $N_B$  - the flux of species B ( $\text{gmole/cm}^2 \text{ s}$ ),
- Nu - Nusselt number  $(D_A k_2 C_{B0})^{1/2}/k_L$  (dimensionless),
- P - the total pressure (bar, torr, kPa, or atm),
- $P_{\text{O}_2}$  - the oxygen pressure in the SOG (torr, mmHg, kPa),
- $\Delta P_L$  - the pressure difference between the reactor inlet and outlet (bar),
- Q - the heat of mixing (kcal or kJ),
- $Q$  - the amount of absorption per unit interfacial area ( $\text{gmole/cm}^2$ ),
- $Q_G$  - the volumetric flow rate of the gas ( $\text{cm}^3/\text{s}$ ),
- $Q_L$  - the volumetric flow rate of the liquid ( $\text{cm}^3/\text{s}$ ),
- R - the ideal gas law constant ( $8.31 \text{ J/gmol K}$ ),
- S - solubility ( $\text{g/kg}$ ,  $\text{mole/kg}$ ),
- $S_v$  - the ratio of gas volume to liquid surface area (cm),
- Sh - Sherwood number  $k_x CL/D$  (dimensionless),
- T - temperature (K or  $^\circ\text{C}$ ),
- U - the overall heat transfer coefficient ( $\text{BTU/hr-ft}^2\text{-}^\circ\text{F}$ ),

- $U_{Cl_2}$  - the chlorine utilization efficiency ( $= \eta_{cl}$ )  
 $V$  - the volume of the jet columns in the SOG reactor ( $cm^3$ ),  
 $V_g$  - the total gas volume of the reactor ( $cm^3$ ),  
 $V_R$  - the volume of the reactor ( $cm^3$ ),  
 $Vol$  - the gas volume over which the transport loss of  $O_2(^1\Delta_g)$  is calculated,  
 $W$  - the laser output power (watts or kilowatts),  
 $W_G$  - the power necessary for gas compression to overcome the system pressure drop,  
 $W_L$  - the hydraulic power necessary for recirculating the liquid through the system,  
 $Y_{dis}$  - the necessary oxygen yield to dissociate iodine (%),  
 $Y_{los}$  - the deactivation by water vapor (%),  
 $Y_o$  - the SOG yield (%),  
 $Y_S$  - the local  $O_2(^1\Delta_g)$  bulk detachment yield (%),  
 $Y_S^0$  - the probability that an  $O_2(^1\Delta_g)$  formed in the liquid will escape to the bulk gas,  
 $Y_{th}$  - the threshold yield (%),  
 $Z_D$  - the concentration-diffusion parameter  $(D_B/zD_A)(C_{B0}/C_A^*)$ ,
- $a$  - the gas-liquid interfacial area per unit volume, or volume specific surface area ( $cm^2/cm^3$ , or  $cm^{-1}$ ),  
 $c$  - the total molar concentration ( $gmole/cm^3$ ),  
 $c_p$  - heat capacity at constant pressure ( $kJ/kg^\circ C$ ),  
 $c_v$  - heat capacity at constant volume ( $kJ/kg^\circ C$ ),  
 $c_1, c_2$  - constants,  
 $d$  - the distance from the surface that diffuse to the surface without deactivation,  
 $h_o$  - the liquid column height in the bubbler SOG (cm),  
 $j_{Ay}$  - the flux of species A in the y direction ( $g/cm^2 s$ ),  
 $k$  -  $= c_p/c_v$ ,  
 $k$  - the reaction rate constant ( $L/gmole\cdot s$  or  $cm^3/mol/s$ ),  
 $k_1$  - the reaction rate constant for  $Cl_2/HO_2^-$  reaction in BHP ( $L/gmole/s$  or  $cm^3/mol/s$ ),  
 $k_2$  - the reaction rate constant for second-order reaction ( $L/gmole/s$ ),  
 $k_4$  - liquid phase quenching rate of  $O_2(^1\Delta_g)$  ( $1/s$ ),  
 $k_6$  - deactivation rate of  $O_2(^1\Delta_g)$  by  $O_2(^1\Delta_g)$  pooling reactions ( $cm^3/mol/s$ ),  
 $k_{d1}$  - the reaction rate constant for energy pooling ( $1/s$ ),  
 $k_{d2}$  - the reaction rate constant for self-quenching ( $1/s$ ),  
 $k_{tot}$  -  $= k_{d1} + 2k_{d2}$ ,  
 $k_c$  - the mass transfer coefficient of chlorine (cm/s),  
 $k_x$  - the mass transfer coefficient (cm/s),  
 $k_G$  - the gas-side mass transfer coefficient (cm/s),  
 $k_L$  - the liquid-side mass transfer coefficient (cm/s),  
 $k_{La}$  - the volumetric mass transfer coefficient ( $1/s$ ),  
 $k_L^0$  - the initial liquid-side mass transfer coefficient (cm/s),  
 $m$  - the total molar gas flow rate ( $gmole/s$ ),  
 $m_c$  - the chlorine molar flow rate ( $mmol/s$ ),  
 $n_{O_2}$  - the total oxygen flow rate ( $gmole/s$ ),  
 $n_{total}$  - the total gas flow rate through the duct ( $gmole/s$ ),  
 $p$  - the partial pressure (atm or bar) of soluble gas in the bulk gas,

- $P_i$  - the partial pressures (atm or bar) of soluble gas at the interface,  
 $r$  - the ratio of  $v^g/v^l$ ,  
 $r_A$  - the rate of reaction of species A (gmole/L/s),  
 $t$  - time or gas exposure time (s),  
 $u$  - mass transfer coefficient (cm/s),  
 $u_1^e$  -  $Cl_2$  mass transfer coefficient (cm/s),  
 $u_3^e$  -  $O_2(^1\Delta_g)$  mass transfer coefficient (cm/s),  
 $u_1^{GI}$  - the gas-transport/interfacial mass transfer coefficient (cm/s),  
 $u_1^{RO}$  - rate-limited  $Cl_2$  mass transfer coefficient (cm/s),  
 $v$  - the gas velocity (m/s),  
 $v^g$  - the gas velocity (m/s),  
 $v^l$  - the liquid velocity (m/s),  
 $x$  - distance into the liquid (cm),  
 $x_A$  - the mole fraction of species A,  
 $y$  - the mole fraction of chlorine,  
 $y_0$  - the mole fraction of chlorine at the SOG inlet,  
 $z$  - number of moles of species B reacting with one mole of species A.
- $\Phi$  - the rate of gas absorption per unit volume of reactor (gmole/cm<sup>3</sup>s),
- $\alpha$  - the  $O_2(^1\Delta_g)$  quenching rate (1/s),  
 $\beta$  - liquid holdup (dimensionless),  
 $\chi$  -  $= (P^2 \cdot n_{O_2} \cdot Vol) / (n_{total} \cdot R \cdot T)^2$ ,  
 $\delta$  - electron flux density (W/cm<sup>2</sup>),  
 $\theta$  - time after the interfacial concentration of liquid-phase reactant falls to zero (s),  
 $\varepsilon$  - the specific surface area of the jet or droplet ( $= S_A/V$ , cm<sup>-1</sup>),  
 $\varepsilon_R$  - the specific surface area of the jet reactor ( $= S_A/V_R$ , cm<sup>-1</sup>),  
 $\gamma$  - probability that gas molecules stick to the liquid BHP,  
 $\eta$  - the fraction of  $O_2(^1\Delta_g)$  molecules reaching the gas-liquid interface,  
 $\eta_c$  - the chlorine utilization efficiency ( $= 1 - y/y_0$ ),  
 $\eta_{ch}$  - the chemical efficiency of COIL system,  
 $\eta_r$  - the chlorine-oxygen conversion efficiency ( $= U_{Cl_2} Y_0$ ),  
 $\eta_{mix}$  - the efficiency of iodine-oxygen mixing,  
 $\eta_{cav}$  - the cavity extraction efficiency,  
 $\mu$  - the viscosity (cP),  
 $v$  - the gas velocity at the gas-liquid interface (cm/s),  
 $\sigma$  - the surface tension of a liquid (dyn/cm),  
 $\varphi$  - the average rate of absorption per unit interfacial area (gmole/cm<sup>2</sup>-s),  
 $\omega_A$  - the mass fraction of species A,  
 $\tau_A$  - the lifetime of  $O_2(^1\Delta_g)$  in solution ( $\mu$ s).

# Singlet Oxygen Generators for Chemical Oxygen-Iodine Laser – A Literature Review

This literature review provides an overview on the technology development, engineering design database, and the state-of-the-art of singlet oxygen generators (SOG) based on the chlorine-basic hydrogen peroxide (BHP) reaction for chemical oxygen iodine laser (COIL) applications. Literature sources for this review primarily consist of scientific journals, SPIE and AIAA proceedings, and U.S. Patents covering the time period from 1977 to 2001. Major sections in this review include: (1) introduction of singlet oxygen and related subjects on the COIL chemistry; (2) singlet oxygen generation based on the chlorine - BHP reaction; (3) singlet oxygen generator designs and typical characteristics; (4) prediction of SOG performance; (5) SOG improvement aspects; (6) other related issues; and (7) appendices including gas-liquid reactor design, chemical/reaction databases, and the results from a U.S. patent search.

## 1. Introduction

### Background

Singlet oxygen generator (SOG) is one of the key components in the chemical oxygen-iodine laser (COIL). The principle of operation for a COIL system is schematically shown in Figure 1. The process starts by contacting gaseous chlorine with basic hydrogen peroxide (BHP) to generate singlet delta oxygen  $O_2(^1\Delta_g)$ . BHP is prepared beforehand by blending concentrated aqueous solutions of hydrogen peroxide and bases. The next step is to transmit collisional energy from metastable  $O_2(^1\Delta_g)$  to the iodine (I) atom ground state. Finally, the excited molecular iodine ( $I^*$ ) is lased to produce 1.315  $\mu\text{m}$  laser beam. The basic COIL hardware includes: (1) the singlet oxygen generator (SOG); (2) the mixing nozzle, in which iodine is introduced to react with the singlet oxygen at a high fluid velocity that may become supersonic; (3) the laser cavity and optics; and (4) auxiliary equipment such as a vacuum pump, heat transfer equipment, a water trap, a chlorine scrubber, and the control system.

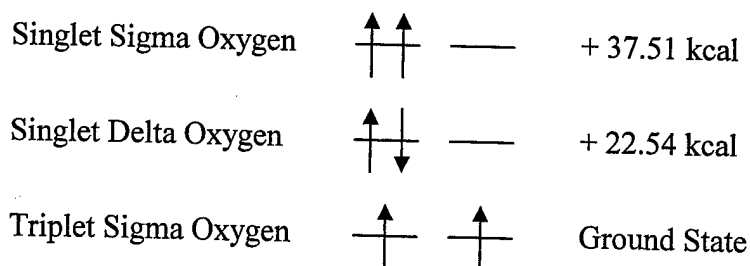
The COIL concept was first demonstrated at the Air Force Weapons Laboratory (AFWL), now the Air Force Research Laboratory (AFRL), in 1977 (McDermott et al., 1978; Benard et al., 1979). Unlike other industrial lasers in which the lasing media are generated either in electric discharges or with radiation produced by electric light sources, COIL is produced by reacting chemical fuels: BHP, chlorine, and iodine. Advances in the enabling technology and performance of COIL devices during the first decade of its existence have been described in several concise reviews covering R&D efforts at Phillips Laboratory, Kirtland AFB, NM (Truesdell and Lamberson, 1992; Truesdell et al., 1994) and at Rocketdyne Division of Rockwell International, Canoga Park, CA (McDoermott, 1992). Since the conception of the first COIL device, the power class of COIL has increased from  $10^2$  W to  $10^4$  W. Similarly, the time period sustainable at the peak power of COIL has been expanded from seconds to minutes. Figure 2 shows the performance of a supersonic COIL at a 10-kW power level sustained over a time period of about two minutes (Naito et al., 1997).

Since COIL has many unique features that are ideal for potential military and industrial applications, R&D activities in COIL reported by international communities have increased considerably in the past 10 years (Chvojka et al., 1992, Bohn, 1993; Zhuang et al., 1994; Nikolaev, 1996; Bohn, 1996; Fujii et al., 1996; Kodymova et al., 1996; Endo et al., 1998). Most of the early reports on the COIL subject (the late 1970's through the early 1980's) were published by researchers in the U.S., Russia, and Japan. The current literature base indicates that there are a number of active COIL R&D programs in the U.S., Russia, Japan, Germany, Israel, Czech Republic, China, India, and South Korea.

The principle of operation and chemistry of COIL are well established as the result of the pioneering work at AFWL and other early Air Force sponsored projects (McDermott et al., 1978; Held et al., 1978; Richardson et al., 1981; Storch et al., 1983). Current efforts for military and industrial applications of COIL focus on the hardware design, testing and scale-up of existing process design concepts. Two significant efforts, funded by the U.S. military, have been the main thrust for the development of COIL systems. The initial ABL effort involves the development of a COIL system that can be fitted into an airplane and operated in mid-air for U.S. Air Force applications (Moler and Lamberson, 1998). A subsequent effort aims at the development of a ground-based chemical laser system, also known as tactical high energy laser (THEL), for the U.S. Army. There are a number of major technical challenges for these developmental efforts. For the airborne laser (ABL) application, the COIL system must be compact, robust, light in weight, and safe to operate in a confined space. In addition, the support facilities for MHP production, quality control/quality assurance, management, storage and transfer of MHP and other chemicals must meet all deployment and military requirements.

### Singlet Oxygen

Oxygen ( $O_2$ ) is known to exist in three possible states, depending on the orbital location and spin direction of its outermost pair of electrons. In its lowest energy level, the two electrons are in different orbitals and have their spins parallel, making the ground state a "triplet",  $O_2(^3\Sigma_g^-)$ . Two other arrangements of these two electrons are possible, resulting in singlet delta state  $O_2(^1\Delta_g)$  and singlet sigma state  $O_2(^1\Sigma_g^+)$ , which are 22.54 kcal and 37.51 kcal above the ground state, respectively.  $O_2(^1\Sigma_g^+)$  is significantly more unstable than  $O_2(^1\Delta_g)$ . The former has a lifetime of 2  $\mu$ s at 1 bar (Bastien and Lecuiller, 1978), whereas the latter has a lifetime of about one hour in the absence of collisions with other molecules (Ogryzlo, 1978). A graphical representation of these three energy states of oxygen is shown below.



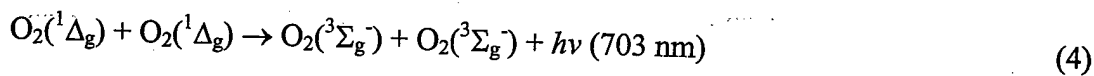
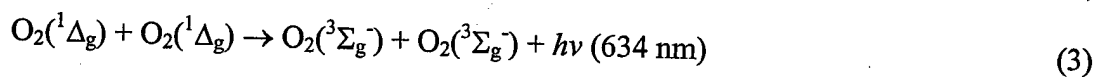
Since  $O_2(^1\Delta_g)$  is the oxygen species involved in COIL, for convenience and simplicity the term "singlet oxygen" used in the context of this paper (such as singlet oxygen generator) refers to singlet delta oxygen denoted as  $O_2(^1\Delta_g)$  unless otherwise indicated.

Isolated molecules of oxygen in the  $^1\Delta_g$  state spontaneously undergo a transition to the ground state, principally through the single molecule (magnetic dipole) transition, known as the monomole emission (Gorman and Rodgers, 1989):



where  $k = 0.935 \text{ h}^{-1}$  which translates to a half-life of 45 minutes (Badger et al., 1965).

When the concentration of  $\text{O}_2(^1\Delta_g)$  is high, two red emission bands, known as the dimole emission, can be observed according to simultaneous transitions given below. The energy difference corresponding to  $\text{O}_2(^3\Sigma_g^-)$  vibrational spacing (Gorman and Rodgers, 1989).



The  $\text{O}_2(^1\Delta_g)$  lifetime can be shortened as the result of collisions with other molecules induced through either an electric-dipole transition at the same wavelength or a radiationless transition to the ground state. This process is known as quenching. Quenching of  $\text{O}_2(^1\Delta_g)$  by various molecules in the gas phase and in solution has been documented (Ogryzlo, 1978; Bellus, 1978; Foote, 1979). For example, in the gas phase at 1 atm the lifetime of singlet oxygen can vary between 1 and  $10^{-5}$ s, depending on the nature of the gas. In solution, the lifetime of  $\text{O}_2(^1\Delta_g)$  may vary significantly with the diluent. For example, the lifetime of  $\text{O}_2(^1\Delta_g)$  has been reported to be 1 ms (in Freon 11), 2  $\mu\text{s}$  (in water) at room temperature, and 5  $\mu\text{s}$  (in BHP) at typical SOG operating conditions (Bonnet et al., 1984). Table 1 shows lifetimes of singlet oxygen in selected solvents (Gorman and Rodgers, 1989). The lifetimes of singlet oxygen may vary significantly when hydrogen atoms in a given solvent molecule are substituted by deuterium or halogen atoms.

**Table 1. Lifetimes of Singlet Oxygen in Selected Solvents**

Solvent	Lifetime ( $\mu\text{s}$ )	Solvent	Lifetime ( $\mu\text{s}$ )
$\text{H}_2\text{O}$	3.8	$(\text{CH}_3)_2\text{C}=\text{O}$	50
$\text{D}_2\text{O}$	62	$(\text{CD}_3)_2\text{C}=\text{O}$	723
$\text{CH}_3\text{OH}$	10	$\text{CH}_3\text{CN}$	62
$\text{C}_6\text{H}_{14}$	31	$\text{CD}_3\text{CN}$	554
$\text{CH}_2\text{Cl}_2$	86	$\text{C}_5\text{H}_5\text{N}$	16
$\text{CHCl}_3$	264	$\text{C}_6\text{H}_5\text{CH}_3$	27
$\text{CDCl}_3$	740	$\text{C}_6\text{D}_5\text{CD}_3$	320
$\text{C}_6\text{H}_6$	30	$\text{C}_6\text{D}_5\text{F}$	1100
$\text{C}_6\text{D}_6$	630	$\text{C}_6\text{F}_6$	3900

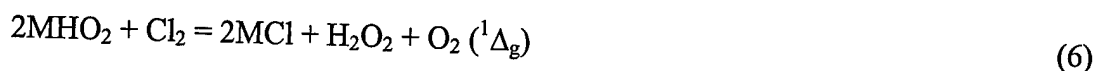
## Chemical Oxygen-Iodine Laser (COIL) Chemistry

The COIL lasing process involves four basic reaction steps according to the sequence shown in Figure 1. The stoichiometry of these reactions is given below.

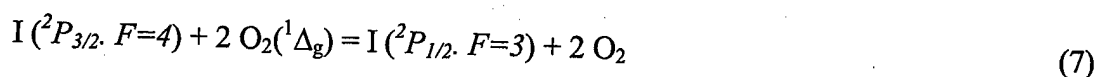
- a. MHP production from alkali hydroxide and hydrogen peroxide aqueous solutions:



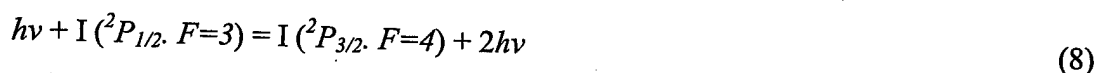
- b. The chlorine-MHP reaction to generate singlet delta oxygen:



- c. Transition of collisional energy from  $\text{O}_2(^1\Delta_g)$  to the iodine (I) atom ground state:



- d. Laser output at 1.315  $\mu\text{m}$  by stimulating emission on the  $F = 3$  to  $F = 4$  hyperfine transition in the spin-orbit split manifold of the  $^2P$  ground term of atomic iodine:



For SOG design considerations, the  $\text{O}_2(^1\Delta_g)$  generation step, eq (6), is the governing reaction that determines not only the stoichiometry of  $\text{O}_2(^1\Delta_g)$  generation, but also types of reactors suitable for the chlorine-BHP reaction.

## Singlet Oxygen Generator (SOG) Requirements

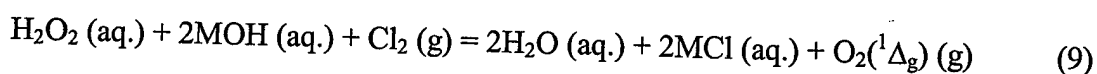
The reaction between gaseous chlorine and aqueous BHP is the most common reaction used for the production of  $\text{O}_2(^1\Delta_g)$ . The characteristic features of this reaction system are three-fold: (1) the rate of this gas-liquid reaction is extremely fast (Held et al., 1978), (2) the lifetime of singlet oxygen in solution is only a few microseconds (Merkel and Kearns, 1972), and (3) the heat of reaction between chlorine and BHP is large (27 kcal/mol  $\text{Cl}_2$ ), which must be rapidly removed for continuous and efficient SOG operation. The BHP solution typically consists of about 60% water. Due to high vacuum condition (typically about 10 torr) in the SOG, significant amounts of water are vaporized. These mass- and heat-transfer characteristics governed by the chlorine-BHP chemistry and reaction conditions determine the basic requirements for SOG design and operation. As will be shown in the following sections, the SOG design can directly and significantly impact on the chemical efficiency of the COIL system. Since an adequate knowledge of general characterizations of gas-liquid reactions and reactors for gas-liquid reactions is beneficial to the understanding of (1) what approach the existing SOGs is based on, (2) why these designs have their reported limitations, and (3) how to identify new approaches that may significantly improve SOG performance, a brief summary of textbook treatment on the subjects of gas-liquid reactions, reactors, and power requirements is provided in Appendix A.

## 2. Singlet Oxygen Generation

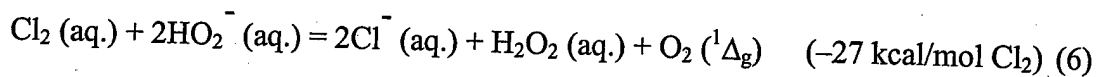
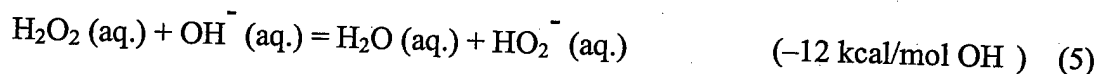
This section addresses the kinetic, thermodynamic, and transport aspects of singlet oxygen generation involving the chlorine-BHP reaction.

### Chlorine-BHP Reaction Mechanism and Kinetics

The reaction between gaseous chlorine and aqueous BHP, such as NaOH + H<sub>2</sub>O<sub>2</sub> or KOH + H<sub>2</sub>O<sub>2</sub>, has been studied by several groups of researchers since late 1970's (Held et al., 1978; Hurst et al., 1978; Kumar and McCluskey, 1987; Ruiz-Ibanez, 1991; Davis et al., 1992). Singlet oxygen is generated according to the following stoichiometry, which is the combination of eq (5) and eq (6).



Since excess hydrogen peroxide is typically used, the concentration of hydroxyl ion is almost zero according to the equilibrium constant ( $K_{\text{eq}} = 4 \times 10^4$ ) for the reaction given by Balej and Spalek (1979). The heat of reaction reported for eq (5) and eq (6), respectively, are given below (Truesdell and Lamberson, 1992).

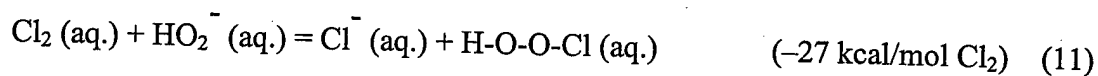


However, the exact mechanism of singlet oxygen production by chlorine absorption into BHP is a matter of controversy (Truesdell and Lamberson, 1992). Several proposed reaction pathways are presented below.

In most of the early works (Held et al., 1978; Sandall et al., 1981), much attention was given to the HOCl-HO<sub>2</sub><sup>-</sup> reaction. These early works identified HOCl + HO<sub>2</sub><sup>-</sup> as the reactive species and proposed the following reaction being the favorable pathway.



However, by contacting chlorine with concentrated BHP solutions, the reaction is postulated to proceed as follows (Ruiz-Ibanez and Sandall, 1991; Davis et al., 1992).



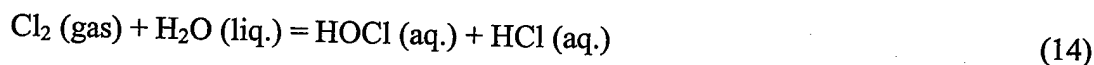
Some of the reported rates of eq (11) are given in Table 2, whereas the rate of eq (12) is reportedly approaching infinity.

Ruiz-Ibanez and Sandall (1991) and Davis et al (1992) reported eq (13) in contrast to their previous publication (Sandall et al., 1981) which described eq (12) as the singlet oxygen production step. It is also postulated that  $\text{Cl-O-O}^-$  reacts spontaneously in the gas phase.  $\text{Cl-O-O}^-$  is expected to decompose fast in the liquid phase, although it can be slightly stabilized by polar solvents (Ruiz-Ibanez and Sandall, 1991).



The  $\text{H}^+$  ion produced from eq (12) is neutralized according to  $\text{H}^+ + \text{HO}_2^- = \text{H}_2\text{O}_2$  and the hydrogen peroxide formed in turn reacts with more hydroxyl ions according to eq (5).

The reactions, eq (9) and eq (6), indicate that the first step of the singlet oxygen generation process involves transforming gaseous chlorine into aqueous chlorine (i.e.,  $\text{Cl}_2(\text{gas}) \rightarrow \text{Cl}_2(\text{aq.})$ ). The solubility of chlorine gas in water at standard temperature and pressure (STP) is reported to be 0.092 gmol/L (i.e., Henry's law constant at STP = 0.092 gmol/kg-bar). Out of this total amount, aqueous chlorine accounts for 0.062 gmol/L. The rest are contributed from other chlorine species such as HOCl (0.030 gmol/L) and chloride (0.030 gmol/L) according eq (14) and possibly  $\text{Cl}_2\text{O}(\text{aq.})$  according to eq (15) if HOCl is not consumed by eq (10).



The equilibrium constant for eq (15) is reported as  $K_{273} = [\text{Cl}_2\text{O}(\text{aq.})]/[\text{HOCl}]^2 = 1/282$  (Renard and Bolker, 1976). It is also known that chlorine becomes more soluble in alkaline solutions, and the hypochlorite ion is remarkably stable in aqueous solution at high pH.

A major side reaction in BHP solutions is the exothermic disproportionation reaction given below. Disproportionation rates of  $\text{HO}_2^-$  and species concentrations at different BHP concentrations were reported (Kumar and McCluskey, 1987).



The reaction rate for the rate-controlling step, eq (6), is given by

$$-d[\text{Cl}_2]/dt = k [\text{Cl}_2][\text{HO}_2^-] \quad (17)$$

where the  $[\text{Cl}_2]$  is the concentration of chlorine (gmol/L) in the aqueous phase. The rate of this reaction is extremely fast. Some of the reported reaction rate constants,  $k$ , are given in Table 2. The reaction is also extremely exothermic ( $\Delta H = -27$  kcal/mol  $\text{Cl}_2$ ), and is believed to yield 100% of the oxygen in the excited singlet state (Held et al, 1978). Richardson et al. (1981) found that the rate of  $[\text{Cl}_2]$  change was not significantly dependent on the hydrogen peroxide concentration ranging from 25 wt% to 85 wt%.

**Table 2. Rates of Reaction between Chlorine and Basic Hydrogen Peroxide**

Rate Constant (m <sup>3</sup> /kg mol s)	Base	Concentration (mol/L)		Temperature (°C)	Reference
		Base	Peroxide		
4.4 x 10 <sup>7</sup>	NaOH	<1	<1	25	Held et al., 1978
> 10 <sup>7</sup>	NaOH	3.5	3 to 26	0	Richardson et al., 1981
2.7 x 10 <sup>7</sup>	NaOH	6	0	0	Sandall et al., 1981*
1.3 x 10 <sup>5</sup>	KOH	4	4	0	Ibanez and Sandall, 1991
5 x 10 <sup>6</sup>	KOH	4	4	12	Davis et al., 1992
2.3 x 10 <sup>7</sup>	KOH	4	4	21	Davis et al., 1992

\* The rate of chlorine hydrolysis in the alkali hydroxide solution.

### Thermodynamic and Transport Properties

The rate expression, eq (17), implies that the reaction, eq (6), is affected by the solubility and diffusivity of chlorine in aqueous hydrogen peroxide solutions. Also, the solubility and diffusivity of oxygen in BHP are critical parameters for singlet oxygen transfer. Experimental values of these properties have been reported by Ruiz-Ibanez et al. (1991). The solubility of chlorine and oxygen in a typical BHP solution in the temperature range of 0°C – 20°C can be expressed as

$$\ln(H_{Cl_2-BHP}) = 28.6389 - 4149.01/T - 0.03758 T \quad (18)$$

$$\ln(H_{O_2-BHP}) = 24.545 - 2586.66/T - 0.02329 T \quad (19)$$

where  $H$  is the Henry's law constant (atm•L/gmol),  $T$  is temperature in Kelyin.

The diffusion coefficient of chlorine in 35% H<sub>2</sub>O<sub>2</sub> aqueous solution in the temperature range of -10°C to 20°C is given as

$$D_{Cl_2-H_2O_2} \text{ (cm}^2\text{/s)} = -1.904 \times 10^{-5} + 8.18 \times 10^{-8}T \quad (20)$$

Similarly, the diffusion coefficient of oxygen in 35% H<sub>2</sub>O<sub>2</sub> aqueous solution in the temperature range of -8°C to 12°C is given as

$$D_{O_2-H_2O_2} = -6.277 \times 10^{-5} + 2.5047 \times 10^{-7}T \quad (21)$$

where  $D$  is the diffusion coefficient in cm<sup>2</sup>/s, and  $T$  is the temperature in K. Diffusion coefficients of a gas in BHP solutions at other concentrations or temperatures can be estimated according to the following semi-empirical equation,

$$D\mu/T = A \exp(E_d/RT) \quad (22)$$

where  $\mu$  is the viscosity (cP),  $E_d$  is a combination of the activation energy for diffusion and viscosity, and  $A$  is determined by the geometric configuration of the diffusing solute gas in the liquid solvent and the partition functions for viscosity. The diffusion coefficients of chlorine and oxygen in typical BHP solutions, as derived from eq (22), are given below.

$$D_{\text{Cl}_2\text{-BHP}} = 1.006D_{\text{Cl}_2\text{-H}_2\text{O}_2} (\mu_{\text{H}_2\text{O}_2}/\mu_{\text{BHP}})\exp(334.8/RT) \quad (23)$$

$$D_{\text{O}_2\text{-BHP}} = 1.006D_{\text{O}_2\text{-H}_2\text{O}_2} (\mu_{\text{H}_2\text{O}_2}/\mu_{\text{BHP}})\exp(337.8/RT) \quad (24)$$

### Chlorine Absorption

Figure 3 shows concentrations of various species at or near the gas-liquid interface in a uniform droplet SOG (Thayer III, 1992). As shown, the concentration of  $\text{O}_2(^1\Delta_g)$  reaches a maximum in the chemical reaction layer, indicating that the yield of singlet oxygen, defined as  $Y_o = [\text{O}_2(^1\Delta_g)]/[\text{Total O}_2]$ , strongly depends on the rates of chlorine absorption and singlet oxygen desorption. Furthermore, Figure 4 shows the predicted changes in the concentrations of the reactants ( $[\text{Cl}_2]$  and  $[\text{HO}_2^-]$ ) with time illustrated by McDermott (1992) derived from the mass-transport equations by Bird et al. (1960).

The absorption of chlorine at the BHP surface is the first step of the chlorine-BHP reaction. McDermott (1992) also reported chlorine mass-transfer coefficient data derived from the early work using the chlorine-sparger technique (Figure 5). In the base concentration ranging from 2.0 mole/L to 10 mole/L, the chlorine mass-transfer coefficient appears to remain fairly constant at  $60 \text{ cm/s} \pm 15 \text{ cm/s}$ . One data point obtained from the jet spray technique shows a significant increase of the chlorine mass transfer coefficient to about  $100 \text{ cm/s}$ .

The chlorine absorption rate has been shown to vary with time, Figure 6 (McDermott, 1992). The initial chlorine absorption rate is proportional to chlorine mass-transfer coefficient. As the time proceeds, the absorption rate becomes limited by the rate of the chlorine-BHP reaction, followed by the rate of base diffusion.

### Oxygen Desorption

The term "desorption" is used here in a broad sense referring to the process of transporting dissolved oxygen from the aqueous phase to the gas phase. The origin of dissolved oxygen in an SOG process may be from two sources. As a result, two types of oxygen desorption occur simultaneously in the SOG process. The first type involves the desorption of dissolved  $\text{O}_2$  gas from the bulk phase of BHP due to the continuous decomposition of hydrogen peroxide, while the second type is the desorption of  $\text{O}_2(^1\Delta_g)$  from the gas-liquid interface where the chlorine-BHP reaction takes place.

The desorption of oxygen resulting from the intrinsic hydrogen peroxide decomposition in the BHP is evident by the formation and rise of tiny bubbles in the BHP during its production and storage. Because of the constant liberation of oxygen within the bulk phase of the BHP, it can be assumed that the BHP is a solution saturated with oxygen. If the pressure

over the BHP is 1 atm, the oxygen concentration in the BHP solution is  $1/H$  atm, where the Henry's Law Constant  $H = 20$  (Nikolaev, 1996). If the pressure decreases as in the SOG process, the BHP solution becomes supersaturated. Excess oxygen enhances the formation of gas bubbles in the bulk liquid phase. The rate of bubble growth is determined by diffusion, and decreases quickly due to deficiency of oxygen adjacent to the bubble layer. The bubbles reach a finite dimension as they rise through the liquid phase and burst into the bulk gas phase. This type of oxygen desorption is a relatively slow process. The accumulation of desorbed oxygen due to the hydrogen peroxide decomposition in the SOG effluent decreases the apparent yield of  $O_2(^1\Delta_g)$ .

The desorption of  $O_2(^1\Delta_g)$  from the gas-liquid interface where the chlorine-BHP reaction takes place has a significantly more impact on the  $O_2(^1\Delta_g)$  yield due to the lifetime of  $O_2(^1\Delta_g)$  in the BHP solution. The rate of desorption of  $O_2(^1\Delta_g)$  must be faster than the rate of  $O_2(^1\Delta_g)$  deactivation typically in the order of microseconds in aqueous solutions. Similarly, the depth (liquid film thickness) from the gas-liquid interface must be small enough to allow for  $O_2(^1\Delta_g)$  desorption from the liquid phase into the gas phase.

Richardson et al (1981) stated that liquid phase quenching will be significant for any  $O_2(^1\Delta_g)$  produced more than 10 molecular diameters from the surface. The expression for the fraction  $\eta$  of  $O_2(^1\Delta_g)$  molecules originating a distance,  $d$ , from the surface that diffuse to the surface without deactivation is given by

$$\eta = (D/d^2 \alpha)^{1/2} [1 - \exp(-1/(D/d^2 \alpha)^{1/2})] \quad (25)$$

where  $\alpha$  is the  $O_2(^1\Delta_g)$  quenching rate and  $D$  is the liquid phase diffusion coefficient for  $O_2$ . The predicted  $\eta$  values, for water and BHP, respectively, as the liquid phase, are given in Table 3. Based on these data, Richardson et al (1981) concluded that the majority of the  $O_2(^1\Delta_g)$  must be produced within  $10^{-6}$  cm of the gas-liquid interface to obtain a high  $O_2(^1\Delta_g)$  yield.

**Table 3. Predicted  $O_2(^1\Delta_g)$  Yield based on Probability Models**

Medium	$D$ (cm <sup>2</sup> /s)	$d$ (cm)	$\alpha$ (1/s)	$(D/d^2 \alpha)^{1/2}$	$\eta$
Water	$2 \times 10^{-5}$	$10^{-6}$	$0.5 \times 10^6$	3.16	0.857
Water	$2 \times 10^{-5}$	$10^{-5}$	$0.5 \times 10^6$	0.316	0.303
BHP	$\sim 5 \times 10^{-6}$	$10^{-6}$	$0.5 \times 10^6$	6.32	0.925
BHP	$\sim 5 \times 10^{-6}$	$10^{-5}$	$0.5 \times 10^6$	0.632	0.502

### Process Efficiencies

The performance of an SOG is described by the  $O_2(^1\Delta_g)$  yield ( $Y_0$ ), which is one of the key parameters to determine the chemical and overall efficiencies of a COIL system. Listed below are several other terms that have also been used to describe  $O_2(^1\Delta_g)$  yield:

- the nascent yield – the yield of  $O_2(^1\Delta_g)$  derived from the chlorine-BHP reaction;
- the detachment yield – the yield of  $O_2(^1\Delta_g)$  as it departs from the solution into the gas stream;
- the plenum yield – the yield of  $O_2(^1\Delta_g)$  prior to iodine injection nozzle; and
- the threshold yield – the minimal  $O_2(^1\Delta_g)$  yield for which positive gain is possible.

In energy terms, critical steps for operating a COIL process have been well defined. Figure 7 shows the allocation of laser output and energy losses in a typical jet-type SOG (McDermott et al., 1997). It is shown that about 30% of the total energy are harvested as laser output. About 40% of the total energy are lost in the SOG operation (i.e., 32% loss in the BHP and 8% chlorine utilization loss). The remaining 30% of the energy losses take place in the COIL system downstream from the SOG.

In a supersonic COIL, the deactivation of  $O_2(^1\Delta_g)$  by energy pooling, eq (26), self-quenching, eq (27), in the subsonic flow upstream of the sonic throat is considered to be an important loss mechanism (Lilenfeld, 1983).



$$k_{d1} = 2.7 \times 10^{-17} \text{ cm}^3/\text{molecule s}$$



$$k_{d2} = 2.7 \times 10^{-17} \text{ cm}^3/\text{molecule s}$$

Auxiliary equipment downstream of an SOG, such as the  $O_2(^1\Delta_g)$  transport duct and water cold trap, may result in further loss due to the wall effect, eq (28).



$$k_{d3} = 2 \times 10^{-5} \text{ cm}^3/\text{molecule s}$$

The  $O_2(^1\Sigma_g^+)$  generated in eq (26) is rapidly quenched back to  $O_2(^1\Delta_g)$  by water, resulting in the net loss of one  $O_2(^1\Delta_g)$ . The overall rate constant for the loss of  $O_2(^1\Delta_g)$  by energy pooling and self-quenching mechanisms is given by  $k_{tot} = k_{d1} + 2k_{d2}$ .

The effect of  $O_2(^1\Delta_g)$  deactivation on the  $O_2(^1\Delta_g)$  yield can be expressed as

$$1/Y = 1/Y_0 + k_{tot} \chi \quad (29)$$

where  $Y_0$  is the  $O_2(^1\Delta_g)$  yield,  $Y$  is the yield at some downstream location, and  $\chi$  is given by

$$\chi = (P^2 \cdot n_{O_2} \cdot Vol) / (n_{total} \cdot R \cdot T)^2 \quad (30)$$

where  $P$  is the pressure,  $n_{O_2}$  is the total oxygen flow rate,  $Vol$  is the gas volume over which the loss is calculated,  $n_{total}$  is the total gas flow rate through the duct,  $R$  is the universal gas constant, and  $T$  is the absolute temperature (K). A lower  $\chi$  corresponds to a lower transport loss of  $O_2(^1\Delta_g)$ . It is convenient to express transport loss of  $O_2(^1\Delta_g)$  in the unit of the product ( $\chi RT$ ) which has the dimensions of pressure\*time.

The chemical efficiency  $\eta_{ch}$  of COIL is expressed by the product of the following local efficiencies (Bohn, 1993):

$$\eta_{ch} = \eta_r(Y_o - Y_{dis} - Y_{th} - Y_{los}) \eta_{mix} \eta_{cav} \quad (31)$$

where  $\eta_r$  is the chlorine-oxygen conversion efficiency,  $Y_{dis}$  is the necessary oxygen yield to dissociate iodine,  $Y_{th}$  is the threshold yield,  $Y_{los}$  is the deactivation by water vapor,  $\eta_{mix}$  is the efficiency of iodine-oxygen mixing, and  $\eta_{cav}$  is the cavity extraction efficiency.

The threshold yield, the minimal  $O_2(^1\Delta_g)$  yield for which positive gain is possible according to the energy exchange equilibrium reaction, is defined as:

$$Y_{th} = 1/[1.5\exp(402/T)+1] \quad (32)$$

where  $T$  is the absolute temperature (K) of the gas at the laser cavity inlet. Based on typical values reported for these parameters, the chemical efficiency is calculated as  $\eta_{ch} = 0.9 \times (0.6 - 0.07 - 0.05 - 0.02) \times 1 \times 0.73 = 0.30$  (Endo et al., 1998). The chemical efficiency of COIL can be also expressed in terms of power output and chlorine flow rate,

$$\eta_{ch} = W/(90.9 \times m_c) \quad (33)$$

where  $W$  is the output power in watts, 90.9 is the energy of iodine emission (kJ/mole  $I^*$ ), and  $m_c$  is the chlorine molar flow rate in mmol/s. Eq (33) implies that the chlorine utilization efficiency is 100%, which can only be approached when using substoichiometric chlorine molar flow rate for a given SOG design. This means that there must be a compromise between high chlorine utilization and minimal  $O_2(^1\Delta_g)$  losses (i.e., high chemical efficiency).

### 3. Effects of Reaction Conditions

Reaction conditions can have a significant impact on the yield of singlet oxygen generation and overall SOG performance. Typical factors that may affect the SOG performance include temperature, pressure, gas-liquid contact time, carrier gas (dilution), reaction media, and BHP formulations. The effects of these factors on the yield of singlet oxygen production are discussed below.

#### Temperature

The temperature at which a SOG process operates can have impacts on COIL system performance in several aspects.

- temperature dependency of the chlorine-BHP reaction
- temperature dependency of singlet oxygen quenching reactions
- rates of water evaporation and water vapor condensation
- change of the gain and saturation intensity

An early study by Richardson et al. (1981) reported that the optimum  $O_2(^1\Delta_g)$  yield was obtained at a cold trap coolant temperature near  $-75^\circ\text{C}$  and a gas temperature near  $-35^\circ\text{C}$ , as shown in Table 4. For a larger-scale cold trap, trap residence time will affect the difference between the gas temperature and the trap temperature, but the data indicated that gas temperatures below  $-40^\circ\text{C}$  will cause significant  $O_2(^1\Delta_g)$  deactivation.

**Table 4. Singlet Oxygen Yield at Various Cryogenic Trap Temperatures**

Coolant Temperature ( $^\circ\text{C}$ )	Gas Temperature ( $^\circ\text{C}$ )	$O_2(^1\Delta_g)$ (%)
-40	-10	44
-73	-35	44
-75	-36	44
-78	-33	49
-87	-53	34
-98	-59	36
-120	-75	26
-146	-83	16
-151	-86	17
...	-88	16
...	-100	10

### Pressure

Although there exist several different types of SOG designs, all of the reported SOG devices operate under high vacuum conditions where the pressure of  $O_2(^1\Delta_g)$  does not, in general, exceed a few torr. The total pressure in the SOG typically ranges from 10 torr to 70 torr. In the Jet SOG design, pressures up to 10 torr are the typical range (Zagidullin et al., 1990). Attempts have been made to increase the operating pressure up to 200 torr without significantly lowering the process efficiency (Adamenkov et al., 1996). For the rotating-disk SOG design, pressures up to 60 torr have been reported (Rittenhouse et al., 1999). As discussed in the section on concentration, lowering pressure results in lower concentration of all species in the process, hence reducing energy losses in terms of  $O_2(^1\Delta_g)$  deactivation due to molecular collisions. However, elevating the process pressure increases the stored energy flow density. The increase in  $O_2(^1\Delta_g)$  density in the resonator working media allows to increase the gain and resonator efficiency. As discussed in the previous section, the most significant energy losses in the working gas mixture are expected to be in the SOG and the iodine mixing area.

Therefore, the selection of SOG operating pressure is one of the most critical design considerations to achieve the optimum  $O_2(^1\Delta_g)$  yield.

### Gas-Liquid Contact Time

The gas-liquid contact time is another critical design parameter. As shown in Figure A-3, gas-liquid contact time requirements determine which experimental technique is best suited for carrying out a given reaction. For  $O_2(^1\Delta_g)$  generation via the chlorine-BHP reaction, it is necessary to achieve the shortest gas-liquid contact time ( $10^{-3}$  s or shorter) at highly expanded surface of interaction. According to Figure A-3, the laminar jet and rotating drum gas-liquid contactors appear to be the basic design options for SOG's.

Ruiz-Ibanez and Sandall (1991) reported chlorine-BHP contact times of 7.72 to 9.43 ms and 2.6 to 2.9 ms, respectively, in the instantaneous and second-order regimes for the laminar liquid jet absorber. Zagidullin et al. (1990) reported a much longer chlorine-BHP contact time of about 100 ms in a Jet-SOG. To satisfy the contact time requirement, velocities of gas and jet must reach certain levels as they flow through the reaction zone. The reported gas velocity at reaction zone outlet typically ranges from 5 m/s to 100 m/s. However, there is a practical limit on gas velocity if aerosol is to be avoided in the output flow. A maximum gas velocity of 37 m/s has been reported in Jet-SOG. The reported jet velocity typically ranges from 3 m/s to 10 m/s.

### Gas Carrier (Diluent) for $O_2(^1\Delta_g)$

Because the lifetime of  $O_2(^1\Delta_g)$  is extremely short in the aqueous phase ( $\sim 5 \mu\text{s}$ ),  $O_2(^1\Delta_g)$  must be isolated as soon as it is generated at the gas-liquid interface. Typically, an inert gas, such as helium, is used as a diluent in the reaction product stream to minimize  $O_2(^1\Delta_g)$  deactivation due to collision with the bulk phase of BHP and water vapor.

Endo et al. (1998) at Tokai University (Hiratsuka City, Japan) in collaboration with Zagidullin et al. of the P.N. Lebedev Physical Institute (Samara, Russia), studied a high-efficiency COIL using nitrogen as the buffer gas. The SOG used in this study was a jet-type design, which will be discussed in the SOG Section. The buffer gas is mixed at just downstream of the exit slit valve. The buffer gas was cooled by passing through a liquefied nitrogen bath. A net chemical efficiency of 23.4% was obtained with cooled nitrogen as the buffer gas. This appears to be the highest efficiency obtained by nitrogen-buffer-gas supersonic COIL reported to date. This value is slightly lower than the highest efficiency of helium-buffer-gas supersonic COIL (29.6%) reported to date. Operating a 2-kW VertiCOIL device with nitrogen as the diluent, a chemical efficiency of 18.5% was achieved by Carroll et al. (2000) at University of Illinois at Urbana-Champaign and STI Optronics, based on a recent work funded by AFRL through Small Business Technology Transfer (STTR) Program.

Rittenhouse et al. (1999) also studied the impacts of helium and nitrogen/helium diluents on the chemical efficiency of COIL performance. The results from this study are summarized in Tables 5 and 6.

**Table 5. Chemical Efficiency as a Function of the He:Cl<sub>2</sub> Diluent Molar Ratio**

Molar Diluent Ratio	Chemical Efficiency (%)	$\chi RT$ (torr-sec)
0:1	3.7	0.21
2:1	19.0	0.068
4:1	21.8	0.055
4.9:1	21.2	0.038
5.7:1	20.2	0.038

**Table 6. Performance Comparison using Nitrogen and Helium as Diluent Gases**

Molar Diluent Ratio	Subsonic Pressure (torr)	Chemical Efficiency (%)	$\chi RT$ (torr-sec)
6:1 N <sub>2</sub> :Cl <sub>2</sub>	95	16.2	0.134
4:1 N <sub>2</sub> :Cl <sub>2</sub>	70	15.4	0.150
2:1 N <sub>2</sub> :Cl <sub>2</sub>	50	11	0.176
4:1 He:Cl <sub>2</sub>	35	24.6	0.040

### Reaction Media

Quenching of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) during its extraction from the BHP solution and quenching of excited atomic iodine I\* by water vapor from the SOG process are well-known parasitic effects in COIL. Vetrovec et al. (2000), at The Boeing Company, Rocketdyne Propulsion & Power, recently demonstrated that both of these effects can be significantly reduced by replacing the hydrogen <sup>1</sup>H<sup>1</sup> isotope (protium) atoms in BHP by the <sup>1</sup>H<sup>2</sup> isotope (deuterium) atoms. In addition to restoring laser power lost to parasitic quenching, the use of basic deuterium peroxide (BDP) is expected to allow generation of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) at elevated temperatures. The approach promises to save refrigerant, reduce the risk of BDP freezing, and delay precipitation of salt from BDP solution. Figure 8 shows the allocation of energy losses in COIL, if the SOG process is operated with BDP instead of BHP. As compared to the allocation of energy losses shown in Figure 7, the laser output increases from 30% to 45.6%, resulting from the significant reduction of loss from 32% in BHP down to 11% in BDP (Vetrovec et al., 2000).

Figure 9 is a graphical illustration of relative power available as the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) flow through various components of 25-kW RotoCOIL system (Truesdell and Lamberson, 1992). The dashed line indicates the power drain if water is not removed from the flow stream. These early works concluded that the real leverages for improving the COIL system are (1) loss reduction in SOG, (2) water removal, and (3) resonator efficiencies.

## BHP Formulation

For a homogeneous BHP solution, its formulation determines the concentration of perhydroxyl ions, which generally reflects the strength of the chemical feedstock for COIL. Selected BHP and MHP formulations are given in Table 7. The effect of BHP formulation on SOG performance is reflected in (1) the formulation strength and energy density, (2) the salt solubility envelop which affects nozzle operations, (3) solid formation during storage, and (4) stability. It has been speculated that a base serves only to supply the hydroxy ions, and its cations take no part in the SOG reactions (Basov et al., 1990). Therefore, a number of alkali or alkaline compounds can be used in the BHP and MHP formulations. The criteria for selecting proper base(s) are based on primarily physical properties of the base(s) and corresponding chloride salt(s) as further discussed below.

**Table 7. Typical BHP and MHP Formulations based on 1 kg Batch Weight**

Recipe	OH <sup>-</sup>	H <sub>2</sub> O <sub>2</sub>	Excess Ratio	H <sub>2</sub> O	LiOH	NaOH	KOH	H <sub>2</sub> O <sub>2</sub>	Reference
	(mole)	(mole)		(kg)	(kg)	(kg)	(kg)	(kg)	
BHP 1	1.48	13.1	8.82	0.496	-	0.0593	-	0.445	McDermott et al., 1978
BHP 2	4.99	7.64		0.46	-	-	0.28	0.26	Blauer et al., 1987
BHP 3	4.99	7.35	1.47	0.47	-	-	0.28	0.25	Truesdell et al., 1992
BHP 4	4 - 8	7 - 9	1.13 - 1.75	0.41 - 0.63	-	-	0.18 - 0.36	0.19 - 0.23	Zagidullin and Nikolaev, 1998
MHP*	4.64	4.83	1.04	0.471	0.0390	0.114	0.141	0.235	Clendening et al., 1999

\* The original formulation was given as base = 5.85 molar, peroxide = 6.09 molar, base molar ratios NaOH/LiOH = 3.0, KOH/LiOH = 2.3 (Assuming MHP density = 1.26 g/cc).

Figure 10 shows the operating line of SOG based on the chlorine-BHP reaction (Hurley and Welch, 2001). As shown, the effective concentration of perhydroxyl ions in BHP is significantly less than the actual concentration of perhydroxyl ions due to the formation of salts and decrease in base concentration. The formation of salts (primarily KCl and NaCl) results in plugging and/or increasing the pressure drop across the nozzle head in Jet-SOG's.

The solubility (S) of alkali metal hydroxides and chlorides exhibits opposite trends as given below.

$$S_{\text{KOH}} > S_{\text{NaOH}} > S_{\text{LiOH}}$$

$$S_{\text{KCl}} < S_{\text{NaCl}} < S_{\text{LiCl}}$$

The addition of LiOH to BHP can increase base strength per unit weight and widen the operating range of MHP since LiCl is soluble in MHP within the practical range of base concentrations. However, the trade-off is how to prevent solid formation in the production of

MHP since LiOH is significantly less soluble than NaOH or KOH. The addition of a second and a third base makes the MHP a five-component solution, and as chlorine is added the number of components becomes eight. Therefore, predicting solid formation envelopes for a given MHP formulation can be extremely difficult. Systematic studies are needed to establish the performance of various MHP formulations.

#### 4. Singlet Oxygen Generators

Since the singlet oxygen generator (SOG) is one of the key components of COIL and the SOG design has a significant impact on COIL performance, extensive effort has been devoted by the U.S. and international researchers in the past 25 years to the development of efficient and compact SOG's. At the same time, the advancement of SOG's coincides with the progress in the COIL development. According to Truesdell et al. (1995), the COIL research and development activities can be divided into five phases:

Phase I	1960 – 1978	Fundamental development leading to COIL
Phase II	1977 – 1984	Subsonic COIL development
Phase III	1982 – 1984	Supersonic COIL lasing demonstration
Phase IV	1984 – 1989	COIL engineering demonstration
Phase V	1990 – 1995	COIL efficiency improvement

Literature published since 1995 has shown that much of the focus of the COIL R&D remains the same as the phase V (COIL efficiency improvement), although the tools and diagnostics technologies used in these efforts have advanced significantly.

In 1992, McDermott, at Rocketdyne Division of Rockwell International, Canoga Park, CA, presented a technology review on the generation of singlet oxygen. McDermott's review (1992) provides a systematic analysis of SOG and analytical approach to the prediction of SOG performance based on four types of SOG designs. Since there appear to have no major breakthroughs in SOG development since 1992, this review has adopted the four basic SOG design categories as originally outlined in McDermott's review except for one minor variation in terminology as shown in parentheses:

- (1) gas-sparger,
- (2) wetted-wall,
- (3) jet, and
- (4) atomizer (spray).

Table 8 summarizes some of the key SOG reactor designs and corresponding power class, measured  $O_2(^1\Delta_g)$  yields, and chemical efficiency reported in the open literature. The chemical efficiency of COIL is defined as the number of emitted photons per number of chlorine molecules passed through the SOG. The highest power class COIL system reported to date is the 25-kW RotoCOIL developed at AFRL, Kirtland AFB (Truesdell and Lamberson, 1992) and the 30-kW twisted-flow aerosol SOG developed at Russian Federal Nuclear Center (Krukovsky et al., 2000). The milestones in the development of SOG for COIL applications are illustrated in Figure 11. The chart shows the time when each of the major types of SOG was first reported, and the time when significant events took place.

**Table 8. Reported Singlet Oxygen Generator Systems for COIL Applications**

SOG Reactor Type (COIL Power)	O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) Yield (Chemical Efficiency)	Developer (Location/Date)	Reference
Cl <sub>2</sub> bubbler/sparger (100 W)	25-40%	AFWL (Kirtland AFB, 1977)	McDermott et al., 1978 Benard et al., 1978
Atomizer nozzles	60-70%	McDonnell Douglas	Richardson et al., 1981
Wetted-column	50%	McDonnell Douglas	Richardson et al., 1981
Roller-drum		Rocketdyne	Sandall et al., 1981
Rotating disk (ICL-II, 4.2 kW)		TRW Corp. (Redondo Beach, CA, 1984)	Truesdell and Lamberson, 1992
Porous pipe (fixed or rotary)	60-70%	Keio University (Yokohama, Japan)	Takejisa et al., 1987
Rotating disk (RotoCOIL, 25 kW)		AFWL (Kirtland AFB, 1987)	Truesdell and Lamberson, 1992
Jet (1.4 kW)	>60%	USSR Acad. of Sciences (Samara, Russia)	Zagidullin et al., 1990 Zagidullin and Valery, 2000
Rotating disk (RADICL, 10 kW)	52%	AFRL (Kirtland AFB, 1991)	Kendrick et al., 1999
Uniform droplet	~60%	STI Optronics, Inc. (Bellevue, WA)	Thayer III, 1992
Rotating disk (VertiCOIL, 2 kW)	~70% (27%)	AFRL (Kirtland AFB, 1995)	Phipps et al., 1995 Rittenhouse et al., 1999
Rotating disk (disk pack) (multi-kW)		DLR (Stuttgart, Germany, 1996)	Bohn, 1996
Rotating disk (mesh-type) (3.7 kW)		DICP (Dalian, China, 1996)	Sun et al., 1996
Twisted-flow aerosol (~30 kW)	45% ~60%	VNIIEPh (Sarov, Russia, 1996)	Adamenkov et al., 1996 Krukovsky et al., 2000
Jet (163 W)	58-88% (18%)	Ben-Gurion University (Beer-Sheva, Israel)	Blayvas et al., 1996
Jet (13.7 kW)	61% (29.6%)	Boeing North American (Canoga Park, CA)	McDermott et al., 1997
Jet (11.3 kW)	50% (18%)	Kawasaki Heavy Industries (Chiba, Japan)	Naito et al., 1997
Jet (230 W)	(10%)	KAERI (Taejon, Korea)	Kwon et al., 1999
Rotating disk (1 kW, estimated)	(15%, est.)	IDSC (Delhi, India)	Mallik et al., 1999

Because of the nature of the chlorine-BHP reaction, the design of efficient gas-liquid reactors (contactors) for singlet oxygen generation hinges on the trade-off between maximizing liquid reactant utilization and minimizing singlet oxygen deactivation. Specifically, the following requirements, Table 9, should be considered for the design and development of a practical SOG.

**Table 9. SOG Requirements and Design Considerations**

<b>SOG Features/ Requirements</b>	<b>Implications</b>	<b>Design Considerations</b>
Concentrated electrolyte solutions	Precipitation of chloride salts and/or alkali hydroxides	<ul style="list-style-type: none"> <li>• Optimize MHP formulations</li> <li>• Develop operating envelopes (phase diagrams) for the working fluid</li> </ul>
Instantaneous reaction at the gas-liquid interface	Diffusion-controlled process	<ul style="list-style-type: none"> <li>• Increase the gas-liquid interface area</li> <li>• Increase the rate of product removal</li> </ul>
Large heat of reaction	Temperature rise in the SOG and MHP	<ul style="list-style-type: none"> <li>• Indirect heat exchange</li> <li>• Evaporative cooling</li> </ul>
Extremely short lifetime of singlet oxygen	Deactivation of $O_2(^1\Delta_g)$ if it is not isolated rapidly at the gas-liq interface	<ul style="list-style-type: none"> <li>• Use a diluent gas, typically helium</li> <li>• Remove water vapor</li> <li>• Lower operating pressure</li> <li>• Shorten gas transport distance</li> </ul>

### **Gas-Sparger Type**

This is the simplest type of SOG designs, which involves intuitively dispersing gaseous chlorine into the bulk BHP solution. Porous materials of various forms have been used as the chlorine sparger.

### Bubbler

The experimental apparatus first used by McDermott et al. (1978) and Benard et al. (1979) to generate singlet oxygen was a simple type of gas-liquid contactors involving a chlorine bubbler (Figure 12) and a chlorine sparger (Figure 13), respectively. The yield of singlet oxygen generation from this type of SOG was reported to be 25% to 40% with a power output of about 100W. Since the dispersed gaseous chlorine rise as in tiny bubbles, this type of gas-liquid contactor is also known as the bubble column reactor (Aharon et al., 1991). The bulk temperature of the liquid phase typically ranges from 260 K to 273 K. The reactor pressure typically is about 10 torr. Helium or argon diluent is premixed with chlorine in a molar ratio typically ranging from 3:1 to 4:1. The effect of diluent ratio up to 30:1 has been studied (Aharon et al., 1991).

The main decay mechanism of  $O_2(^1\Delta_g)$  in the bubbler-type SOG is the dimole emission (eq 3 and eq 4). The rate of the dimole emission increases with the hydrostatic pressure of the liquid in the chlorine-BHP reaction system. Some of the early data on the bubbler SOG, as originally compiled by Basov et al. (1990), are given in Table 10. In these studies, the oxygen

partial pressure in the SOG ranged from 0.3 mmHg (torr) to about 3 mmHg (torr), and liquid column height ( $h_o$ ) ranged from 4.5 cm to 9.9 cm. The data show that the  $O_2(^1\Delta_g)$  yield increases as the liquid column height is reduced. It has been suggested that the performance of the bubbler SOG at higher operating pressure may be achievable by reducing the liquid column height, increasing the reactor cross section area, and employing means to prevent the solution from being carried away by the gas flow. The operating pressure for the bubbler SOG is limited by a level of about 10 mmHg (Basov et al., 1990).

**Table 10. Operating Conditions and Performance of the Bubbler SOG**

$O_2(^1\Delta_g)/O_2$ (%)	$P_{O_2}$ (mmHg)	$h_o$ (cm)	Reference
35-40	0.975	4.5	McDermott et al., 1978
35	0.975	9.9	Benard et al., 1979
20-40	-	-	Richardson and Wiswall, 1979
44	0.323	7.9	Bachar and Rasenwaks, 1982
<44	2.475	7	Watanabe et al., 1983
<50	0.3	-	Bonnet et al., 1984
35-45	1.275	-	Grigor'syev et al., 1984
40	0.375	7.1	Vagin et al., 1984
51-64	0.75-0.3	-	Watanabe et al., 1986
>50	1.8	8.5	Yoshimoto et al., 1986
40	0.25	~10	Aharon et al., 1991

#### Fixed Porous Pipe

Porous pipe designs are variations based on the simple disk sparger. Takehisa et al. (1987) at Keio University (Yokohama, Japan) studied SOG designs involving fixed and rotary porous pipes, respectively. In these designs, the reaction takes place in the thin layer of the BHP solution formed on the surface of the porous pipe. The  $O_2(^1\Delta_g)$  generating area is separated from the chlorine input area by the thin liquid layer, so chlorine is well utilized and the  $O_2(^1\Delta_g)$  is diffused to the gas phase at once. As shown in Figure 14, the porous pipe is made of silica ceramics with an average pore diameter of 4-5  $\mu\text{m}$ . The outside diameter (O.D.) of the porous pipe is 10 mm, and the length of the porous section is 250 mm. Glass tubes are attached to both ends of the porous pipe. The BHP solution is introduced from a perforated stainless steel tube (O.D. = 6.35 mm) located 10 mm above the porous pipe. The orifices of the tube are 5 mm in diameter, spaced at intervals of 5 mm, and facing the porous pipe. Results from this study show that the yield of singlet oxygen generation is enhanced by about 10% as compared to that obtained from the simple sparger bubbler SOG.

#### Rotary Porous Pipe

Figure 15 shows the rotary porous pipe SOG design studied by Takehisa et al. (1987). The porous pipe is made of carbon with an average pore diameter of 10  $\mu\text{m}$ . The O.D. and length of the porous section are 70 mm and 200 mm, respectively. The gaseous chlorine is introduced through the hollow shaft (stainless steel), which has several holes at the section extended from the reaction vessel. This rotating shaft is supported by Viton O-rings. Results

show that the yield of singlet oxygen generation obtained by the rotary porous pipe SOG is slightly lower than the yield obtained from the fixed porous pipe SOG. The porous materials and pore sizes used in both of these apparatus are summarized in Table 11.

**Table 11. Porous Materials and Pore Size used in the Porous Pipe SOG Studies**

Material	Major Component	Average Diameter of the Pores ( $\mu\text{m}$ )	Comment
Ceramics	$\text{SiO}_2$	4-5	Good
Ceramics	C	10	Good
Ceramics	C	110	Pore size too large
Porous glass	$\text{SiO}_2$	3	Pore size too small
SS 316	Fe, Cr, Ni	5	Corroded by chlorine

### Wetted-Wall Type

The wetted-wall type SOG designs include (A) the falling-film (or wetted-column) design, (B) the roller-drum design and (C) the rotating-disk (disk-pack) design. One of the key features of these designs is the creation of a thin film of the BHP solution on a stationary or moving surface, followed by contacting gaseous chlorine with the BHP film.

#### Falling-Film Design

Richardson et al. (1981) studied the first type of the wetted-column SOG designs (Figure 16). The SOG inlet consisted of 424 reaction tubes (each with 8-mm O.D. and 6-mm I.D.). The BHP solution is gravity-fed at the inlet. A thin film of the BHP solution is formed as the solution is falling along the internal surface of each tube. Gaseous chlorine is blown through the center of each tube.

This falling-film SOG design can be described by a simple scaling model since the gas-liquid interaction area is reasonably well defined, provided that the liquid flow in the individual tubes is assumed to be laminar. Richardson et al. (1981) also compared wetted-column SOG designs with the spray nozzle designs. To increase chlorine utilization, the reaction columns should be longer than a certain length, which is normally about 10-20 cm. Singlet oxygen generated at the inlet of a column is likely to be deactivated when transported through the column. Therefore, the wetted-column design gave a lower singlet oxygen yield than that obtained from the atomizer nozzle design (Richardson et al., 1981).

#### Roller-Drum Design

Sandall et al. (1981) at Rocketdyne Division of Rockwell International reported an SOG apparatus based on the roller-drum design (Figure 17). The BHP solution entered the vacuum reactor through a Teflon nozzle and wetted roller 2 which was directly geared to the large roller 1 such that their surface speeds were matched. The wetted surfaces of both rollers were made of high density aluminum oxide. The gap between the rollers was variable and kept at approximately  $5.1 \times 10^{-4}$  m (0.020 inch). By controlling the BHP flow rate, roller speed, and

the roller gap, a layer of base of even thickness and width could be applied to the large roller. Roller 1 had a diameter of 0.101 m and was actively cooled to 0°C with a methanol/water mixture, which was circulated beneath the aluminum oxide sleeve.

### Rotating-Disk (Disk Pack) Design

Early work on the rotating-disk SOG design began around 1990. Some of the reports published recently on VertiCOIL and RADICL are the result from these early studies. Harpole et al. (1992), at TWR (Space and Technology Group), Redondo Beach, CA, initially reported the design and performance results of a 35-kW rotating disk SOG. A 3-D schematic of this rotating SOG is shown in Figure 18. The wetted components of this system were made of Nickel, Inconel 718, and Teflon, which are reportedly among the few materials found compatible with both BHP and chlorine. Figure 19 shows the liquid separator employed in the COIL system between the rotating disk generator and impurity cold trap. Typical results derived from this system are summarized in Table 12. The BHP used in the tests was made from mixing 90% H<sub>2</sub>O<sub>2</sub> and 50% KOH solutions and distilled water, and had a final composition of 7 M KOH and 1.5:1 H<sub>2</sub>O<sub>2</sub>:KOH molar ratio. As shown in Figure 20, at a chlorine flow rate of less about 0.4 gmole/s, the chlorine utilization efficiency is nearly 100%. As the chlorine flow rate increases, the chlorine utilization efficiency decreases by about 10%.

**Table 12. TRW Rotating SOG Hot Flow Performance Summary**

Test No.	166.8	166.10	173.3	173.6	173.7	177.6
He Flow (mol/s)	0.99	0.98	1.02	1.04	1.45	0.94
Cl <sub>2</sub> Flow (mol/s)	0.43	0.48	0.73	0.73	0.73	0.47
Cl <sub>2</sub> Utilization (%)	98	96	88	87	90	92
<b>In the Diagnostic Duct</b>						
Total Pressure (torr)	19	27	37	35	39	22
H <sub>2</sub> O Partial Pressure (torr)	1.8	1.7	1.9	0.8*	1.0*	0.7*
Total O <sub>2</sub> Partial Pressure (torr)	5.2	8.1	12.9	12.2	11.5	6.5
O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) Partial Pressure (torr)	3.6	5.2	6.8	6.6	6.8	4.3
O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) Fraction	0.69	0.64	0.53	0.54	0.59	0.66
Maximum Power in the Flow (kW)	27.2	27.9	31.7	32.7	36.5	27.2
Power/Unit Cross-Section Flow Area (W/cm <sup>2</sup> )	135	138	157	162	181	135

\* Impurity cold trap refrigeration system on.

Rittenhouse et al. (1999), at U.S. Air Force Research Laboratory, Kirtland Air Force Base, Albuquerque, New Mexico, developed a high-efficiency 5-cm gain length supersonic COIL as shown in Figure 21. VertiCOIL is a 2-kW class supersonic COIL driven by a small rotating-disk SOG. A close-up schematic of the rotating-disk SOG is shown in Figure 22. The generator housing is composed of high-density polyethylene and contains sixteen 10-in-diameter disks (G-10 fiberglass or nickel). The 16 disks (0.031 in thick each) form a 2-in-wide disk pack, with a spacing of 0.093 in between disks. The disk pack is controlled at a rotating speed of 45 RPM during lasing to continuously supply fresh BHP to react with chlorine. Chlorine is delivered to the generator through a 0.5-in-diameter stainless steel tube with a row of 35 0.05-in-diameter holes drilled in a zigzag pattern down its 2-in length. Teflon scrapers

with a thickness of 0.093 in to match the disk spacing, are installed to remove the warm, partially depleted BHP from the rotating disks.

To manage the heat generated from the chlorine-BHP reaction and minimize the amount of water vapor generated, VertiCOIL was designed to recirculate BHP to allow long run times. Up to 50 L of BHP was prepared from 45 wt% KOH and 70% H<sub>2</sub>O<sub>2</sub>, yielding a perhydroxyl anion (HO<sub>2</sub><sup>-</sup>) concentration of 7.5 M. A Viking fixed gear pump located directly below the mixing tank circulated the BHP at 6 gal/min. The BHP was pumped through a Spirec Model K4T heat exchanger (15 ft<sup>2</sup> of fluid surface area) to remove the heat liberated from the chlorine-BHP reaction. The coolant used in the cold side of the heat exchanger was Dow Corning Syltherm XLT (dimethyl polysiloxane). The Syltherm fluid was maintained at -30°C through direct contact cooling with liquefied nitrogen in a separate tank. VertiCOIL reportedly produced an average power of 1730 W at chlorine flow rate of 70.8 mmol/s, primary He diluent flow rate of 280 mmol/s, and pressure of 60 torr. The highest chemical efficiency of the process was 26.9%, and the highest chlorine utilization efficiency was 98%.

A 10-kW class supersonic COIL (RADICL) was reported by another group of researchers at Kirtland AFB (Kendrick, 1999). Figure 23 is a cut-away diagram of RADICL showing the rotating-disk SOG and the transition and diagnostic ducts. RADICL employs an 18-in-diameter rotating disk SOG and a 1.42-cm x 25.4-cm single-slit supersonic nozzle. The transport volume from the disk-pack exit to the optical port of the oxygen-diagnostic duct is 5.5 L. The gas volume available to the flow within the disk pack (assuming a BHP film thickness of 3.5 mm) is approximately 8 L. Multi-pass absorption experiments on RADICL were conducted to determine SOG efficiency, which is summarized in Table 13. Using the same SOG module (on loan from AFRL, Kirtland AFB) from RADICL, Grunewald et al. (1998) at Institute of Technical Physics (DLR) studied effects of gas mixing on a similar 10-kW COIL. Figure 24 shows the photo and sketch of DLR COIL. Figure 25 shows the overall layout of the rotating-disk SOG with the closed BHP circuit, gas supply and gas diagnostics (Duschek et al., 1998). The rotating-disk design was modified with the addition of 12 blades as shown in the insert of Figure 26.

**Table 13. Singlet Oxygen Yield Results on RADICL under Various Conditions**

Test Type	Diluent Ratio (He:Cl <sub>2</sub> )	Disk Speed (rpm)	BHP Temp (°C)	O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) Yield (%)
Baseline	3:1	20	-17.7	52
High BHP Temperature	3:1	20	-7.9	52
High BHP Temperature	3:1	20	-12.6	53
High Disk Speed	3:1	25	-17.5	53
High Disk Speed	3:1	30	-19.1	54
Increase BHP Level 3 L	3:1	20	-17.9	53
Decrease BHP Level 3 L	3:1	20	-17.9	53
Increase Diluent	4:1	20	-17.9	56

Dickerson et al. (1992) presented a detailed work on modeling the rotating disk SOG. In general, the performance of rotating-disk SOG's depends on disk surface area, disk spacing, and rotating speed. Increasing the surface spacing reduces the overall mass transfer coefficient as gas side resistance increases causing the generator utilization to fall. Larger generator volume for a given surface area (i.e., using a larger disk spacing) leads to an increase in the residence time which reduces the singlet oxygen yield due to the energy pooling reaction. However, decreasing surface spacing or disk spacing beyond a point is practically limited by film stripping and gas entrainment. The exposed surface area of disks is in the range of 7 to 10 ft<sup>2</sup>/kW of laser power.

Studies on the rotating-disk SOG were reported by other researchers including Sun et al., (1996) at Chinese Academy of Science (CAS), Dalian Institute of Chemical Physics (Dalian, China), and Mallik et al. (1999) at Defense Science Center (Delhi, India) (IDSC). Critical design parameters for the rotating-disk SOG reported by early works and recent studies are listed in Table 14. The examples include those reported by TRW (Harpole et al., 1992), VertiCOIL (Rittenhouse et al., 1999), RADICAL (Kendrick, 1999), IDSC (Mallik et al., 1999), and CAS (Sun et al., 1996).

**Table 14. Typical Dimensions for Rotating-Disk Pack SOG**

Parameter	TRW	VertiCOIL	RADICL	IDSC	CAS
Disk diameter (inch)	15	10	18	10	
Number disks	57	16	-	13	
Disk spacing (cm)	0.25	0.24	-	0.25 - 0.3	
Disk thickness (cm)	0.089	0.079	-	-	
Disk rotating speed (rpm)	20	25 - 45	20 - 30	45	40 - 60
BHP volume (Liter)	28				30
Power (kW)	35	2	10	1	7
Power/SAGR* (kW/(m <sup>2</sup> /s))	8.1	3.0-5.3		1	

\* SAGR – surface area generation rate = (total surface area of the disk pack) x rotating speed.

### Jet Type

The jet SOG design, first suggested by Balan et al. (1989) as a new technique for singlet oxygen production, refers to injecting a single or array of liquid BHP jet(s) downwards into a reaction zone where gaseous chlorine is injected co-currently, perpendicularly, or counter-currently. The increase in the pressure of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) and the chlorine utilization efficiency in a jet SOG requires optimization of the parameters of the generator, such as, the time of contact between the chlorine and the jets, the velocity of the jets, their specific surface area, and the geometric parameters of the jet SOG.

In 1990, Zagidullin et al., at Kuibyshev Branch of the Academy of Sciences of the USSR (Samara, Russia), reported test results on a continuous-flow JSOG. The experimental setup consisted of a jet generator, a vacuum pump with a nitrogen trap, a system for measuring

the concentration of  $O_2(^1\Delta_g)$  and  $Cl_2$ , the mass consumption of  $Cl_2$ , the pressure of the gaseous mixture, and the temperature of the working BHP solution. The Jet SOG was made of vertical glass tube 40 cm long with an I.D. of 5.6 cm. In the upper part of the tube an injector was placed, forming a uniform flux in a jet of the solution, with the jet diameter of 0.3 mm. For a jet consisting of 250 orifices in the injector the specific surface area of the jet reactor,  $\epsilon_R = A_S/V_R$ , was  $1\text{ cm}^{-1}$ , where  $A_S$  is the total area of the jet and  $V_R$  is the volume of the reactor. If the number of orifices equals to 520,  $\epsilon_R$  became  $2\text{ cm}^{-1}$ .

The BHP solution was fed into the injector through the electromagnetic valve from a cooled vessel of volume 1.5 liters. The pressure in the vessel could be varied and maintained anywhere between 0 and 1 atm. A similar vessel was attached to the lower end of the tube to collect the solution. The chlorine was fed into the generator from a 10-liter cylinder of gaseous chlorine through an aperture in the upper part of the lower volume and was pumped through the reactor in the opposite direction to the jet. The volumetric rate of pumping in the Jet SOG was 21 liters/s. The mass consumption of chlorine was determined from the rate of decrease of the chlorine pressure in the cylinder. The BHP solution was made from 1 liter of 30%  $H_2O_2$  and 0.25 liter of a 12N solution of KOH cooled to  $-10^\circ\text{C}$ . The velocity of the jet was 7 m/s. The consumption of the solution was  $130\text{ cm}^3/\text{s}$  for  $\epsilon = 1\text{ cm}^{-1}$ , and  $250\text{ cm}^3/\text{s}$  for  $\epsilon = 2\text{ cm}^{-1}$ . The time of contact between chlorine and the jet was  $\sim 100\text{ ms}$ . The experimental results showed that it was possible to obtain a pressure of  $O_2(^1\Delta_g)$  of  $\sim 10$  torr with a high concentration ( $>60\%$ ) in the medium. The residual chlorine pressure decreases with increasing gas-liquid contact area.

A similar JSOG design was further studied by Zagidullin in collaboration with the researchers at Ben-Gurion University of the Negev (Beer-Sheva, Israel) (Blayvas et al., 1996). Figure 27 shows a schematic of the JSOG used in this reported study. The JSOG was manufactured of Plexiglass for visual observation of the BHP/ $Cl_2$  reaction. The reaction zone is 20-cm long with 12-mm x 50-mm cross section. The BHP solution is prepared in a stainless steel tank (2) with a volume of 7.5 liters, and is delivered into the JSOG reaction zone under atmospheric pressure through two 1-cm I.D. polyethylene tubes. The BHP jets are generated in the reaction zone through a perforated plate (3). Details for the two types of perforated plates used in this study are provided in Table 15. Test conditions and results, in terms of the yield of  $O_2(^1\Delta_g)$  and  $Cl_2$  utilization ( $\eta_{Cl}$ ), obtained from operating these two JSOG configurations are summarized in Table 16. More results from the same research lab were reported later by Rosenwaks et al. (1997).

**Table 15. Perforated Plate Designs of JSOG for Liquid Jet Generation**

Jet Plate	Perforated Plate Dimensions	$Cl_2$ Flow Rate (mmole/s)	BHP Flow Rate (Liter/s)
#1	74 tubes of 10-mm length and 0.6-mm I.D. 17 tubes of 23-mm length and 0.8-mm I.D.	10	0.2
#2	86 holes of 2.5-mm length and 0.7-mm I.D. 20 tubes of 23-mm length and 0.8-mm I.D.	20	0.32

**Table 16. Results from the Operation of the Jet SOG (Blayvas et al., 1996)**

Jet Plate	Gas Velocity (m/s)	Reaction Zone Pressure (torr)	Cl <sub>2</sub> :He molar ratio	Y (%)	$\eta_c$
#1	12.8	28	1:0	68	0.92
#1	11.7	52	1:1	67	0.90
#1	10.4	90	1:1.8	58	0.92
#2	21	29	1:0	88	0.94
#2	22.8	58	1:0.9	84	0.95
#2	21.7	91	1:1.9	80	0.95

Spalek and Kodymova (1996), at Institute of Physics of the Academy of Sciences (Prague, Czech Republic), reported data derived from a systematic JSOG study on the influence of jet injector configurations on the performance of Jet SOG. Cross-section views and dimensions of five jet injectors are shown in Figure 28. Results from experiments using two gas velocities are given in Table 17.

Schall and Kraft (1996), at DLR – Institut für Technische Physik, Stuttgart, Germany, studied liquid breakup in JSOG under simulated conditions. The maximum intact jet length was found at a driving pressure of about 3 bar, and was about 25 cm. For higher pressures the instability of the jets increased rapidly. The jets showed considerable surface spraying and a reduced intact length. For a sprayless operation the packing density is limited by a volume specific area  $\epsilon = 12$  to  $15 \text{ cm}^{-1}$ .

McDermott et al. (1997) reported results on a high throughput Jet SOG with both cross-flow (Figure 29) and counter-flow (Figure 30) configurations. These designs appear to be more compact than conventional Jet-SOG systems. Typical reported test conditions involve 0.25 mole/s Cl<sub>2</sub>, 0.75 mole/s H<sub>e</sub>, 0.005 mole/s I<sub>2</sub>, 0.25 mole/s secondary H<sub>e</sub>, 12.7 cm gain length, 100 torr generator pressure, 33 torr plenum pressure, and 3 torr at Laser cavity. Process conditions for operating the counter-flow Jet-SOG at two chlorine flow rates are given in Table 18. A chemical efficiency of 29.6% was reported using this new and improved Jet SOG.

**Table 18. Process Conditions for the Counter-Flow Jet-SOG**

Parameter	Unit	0.25 mole/s Cl <sub>2</sub>	0.50 mole/s Cl <sub>2</sub>
Generator Volume	Liter	0.80	3.2
$\epsilon$	cm <sup>-1</sup>	8.95	5.06
BHP Molarity	mole/L	7.2	7.2
Cl <sub>2</sub> Inlet Pressure	Torr	22	21
Gas Velocity	m/s	34	37
Liquid Velocity	m/s	6.3	10
K <sub>c</sub>	cm/s	52	75

Table 17. Results from JSOG Experiments at Two Different Gas Velocities

O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) yield and residual chlorine content for gas velocity 15 m.s <sup>-1</sup> , jet velocity, v <sub>j</sub> , and pressure in generator 1.5 kPa and 6 kPa					
Type of jet injector	v <sub>j</sub> (m.s <sup>-1</sup> )	O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) yield (%)		residual Cl <sub>2</sub> content (%)	
		1.5 kPa	6 kPa	1.5 kPa	6 kPa
03-6	3.5	82	~ 62	10	20
05-5	6.3	70	62	5	19
05-3	6.3	78	60	12	30
08-4	6.8	79	~ 68	10	~ 26
F03-3	5.8	83	> 63	14	~ 45

O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) yield and residual chlorine content for gas velocity 6 m.s <sup>-1</sup> , jet velocity, v <sub>j</sub> , and pressure in generator 1.5 kPa and 6 kPa					
Type of jet injector	v <sub>j</sub> (m.s <sup>-1</sup> )	O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) yield (%)		residual Cl <sub>2</sub> content (%)	
		1.5 kPa	6 kPa	1.5 kPa	6 kPa
03-6	3.5	75	56	5	15
05-5	6.3	60	51	1	10
05-3	6.3	65	52	8	24
08-4	6.8	67	~ 51	5	14
F03-3	5.8	69	63	2	26

Water content in output gas from JSOG			
Type of jet injector	Jet dimens. (mm)	Distance of rows (mm)	water content (%)
03-6	ø 0.3	1.4	4 - 16
05-5	ø 0.5	1.6	3 - 12
05-3	ø 0.5	3.0	2 - 6.5
08-4	ø 0.8	2.0	2 - 9.5
F03-3	3 × 0.2	2.5	2 - 8.5

Kwon et al. (1999) at Korea Atomic Energy Research Institute (Taejon, Korea) recently reported a Jet SOG study based on the conventional design. The Jet SOG was made of transparent material having a transverse cross section of  $20 \times 100 \text{ mm}^2$  and a reaction height of 100 mm. The BHP solution was prepared from 20 L of 50 wt% hydrogen peroxide and 20 L of 43 wt% KOH solution, and stored in the mixing tank at a temperature of  $-15^\circ\text{C}$ . The BHP was brought to the Jet SOG by vacuum transfer and was injected into the Jet SOG through jet injection nozzle. A collection tank was used to receive the reacted BHP solution located under the Jet SOG (i.e., no recirculation of BHP). A perforated plate consisting of 196 holes with a diameter of 0.8 mm was used as the BHP jet injection nozzle. The BHP jet flow rate was about  $820 \text{ cm}^3/\text{s}$ .

### Atomizer Type

The atomizer-type SOG is designed to increase the gas-liquid interface by creating fine droplets or aerosols of liquid BHP. The creation of fine droplets or aerosols of a liquid in contact with a gas can be accomplished by using an ejector or an eductor.

Since the early 1980's, various spray-nozzle and nozzle-array designs have been explored for SOG applications. Spray-nozzles or nozzle-arrays are typically associated with the jet-type and atomizer-type SOG's. Major challenges involve the design and fabrication of spray nozzles, chlorine flow pattern and velocity control, and minimization of  $\text{O}_2(^1\Delta_g)$  losses.

### Gaseous Chlorine Motivated

Richardson et al. (1981) at McDonnell Douglas Research Laboratories, studied several SOG designs utilizing spray nozzles to promote the atomization of liquid BHP by the flow of gaseous chlorine. One of the spray nozzle SOG designs, which display relatively high efficiencies, is shown in Figure 31. The chlorine injector is positioned either at or just below the liquid level in the BHP solution reservoir, so that the momentum of the chlorine jet entrains liquid droplets into a reaction tube. The four-tube chlorine injector was constructed of Pyrex. Excess BHP vapor was removed with a re-entry trap immersed in an ethanol cooling bath. The temperature of the bath was controlled by regulating the flow of liquid nitrogen through a copper cooling coil immersed in the ethanol. The reported data indicate that the optimum singlet oxygen yield is obtained at a trap coolant temperature near  $-75^\circ\text{C}$  and a gas temperature near  $-35^\circ\text{C}$ . For a large-scale trap, trap residence time will affect the difference between the gas temperature and the trap temperature, but the data indicate that singlet oxygen deactivation became significant at gas temperatures below  $-50^\circ\text{C}$ .

Several atomizer nozzles utilizing commercial designs were also tested. These nozzles produced a fine mist of droplets ( $\sim 1 \text{ mm}$  diameter) at atmospheric pressure. However, when the nozzles were used at low pressure ( $\sim 1 \text{ kPa}$ ), the NaOH precipitates as the drops vaporize which provides nucleation centers for the droplets and reduces the effectiveness of the atomizer. The critical factors for nozzle designs involve the enhancement of fine mist production at low pressures to increase the chlorine utilization. At high pressures the singlet oxygen yield was very low.

## Aerosol SOG

The aerosol SOG concept is based on the generation of fine droplets of liquid BHP that increases the interface contact area between chlorine gas and liquid BHP. As shown in Table A-2, the total surface area of one liter liquid in 15  $\mu\text{m}$  diameter droplets is 400  $\text{m}^2/\text{L}$  as compared to 6  $\text{m}^2/\text{L}$  for the same amount of liquid in 1000  $\mu\text{m}$  diameter droplets. The increased surface area of the liquid BHP in the form of fine droplets may have a significant and positive impact on both the chlorine utilization efficiency and the  $\text{O}_2(^1\Delta_g)$  yield. As illustrated in Figure 32, there is a progressive transition in flow patterns of BHP from ideal liquid jets to aerosol generation (Schall and Kraft, 1996).

Early attempts were made by Davis (1987) and Hed (1990) to explore the potential of utilizing an aerosol of liquid BHP in contact with gaseous chlorine. Blauer et al. (1987) studied an aerosol SOG involving parallel aerosol and chlorine flows in the reaction zone followed by separating the aerosol from singlet oxygen in a twisted flow pattern in a separator underneath the reaction zone. Schematic of aerosol test apparatus and coaxial pentad injector element developed by Blauer et al. (1987) are shown in Figure 33 and Figure 34, respectively. Correlated aerosol test results using different injector elements are shown in Figure 35. Projected SOG system performance in terms of the concentrations of major species is plotted in Figure 36. Thayer III (1992) developed a uniform droplet SOG as shown in Figure 37. Some of the features of uniform droplet SOG are similar to those of jet-SOG.

Adamenkov et al. (1996), at Russian Federal Nuclear Center (VNIIEF), developed a hybrid SOG design trying to take advantage of the merits associated with the aerosol and jet SOGs. As shown in Figure 38, the reactor has a cylindrical casing and a rotating auger with a perforated shaft. Gaseous chlorine flow is directed along the cylinder. The BHP solution is injected through the center of the shaft, and is distributed by the perforated holes in the aerosol or jet form perpendicularly to the gas flow. As the auger rotates, the flow of the liquid is twisted in the reaction zone so that singlet oxygen can be separated from aerosol immediately after the reaction. Specific interaction surface is estimated to be 40  $\text{l}/\text{cm}$ . This SOG design offers possibility to raise gas velocity and pressure while maintaining high chlorine utilization efficiency. Figure 39 shows the differences in system configurations of the hybrid JSOG and the JSOG reported by Zagidullin et al. at Samara, Russia (1990). Results from these two studies are compared in Table 19. A most recent publication by the same research group (Krukovsky et al., 2000) indicates that significant modifications have been made. Both chlorine and BHP injection ports have been relocated to the bottom the SOG in the new design as shown in Figure 40. A photo of this twisted flow aerosol SOG test setup is shown in Figure 41.

The aerosol SOG concept has also been pursued by researchers at TWR. Clendening and Hartlove (1998), at TRW Space & Electronics Group (Redondo Beach, CA), reported a COIL performance model (ICONOS – Integrated COIL Optics Nozzle SOG with both one and two dimensional model versions) to predict end-to-end performance of COIL systems, including systems based on the aerosol SOG concept.

**Table 19. Comparison of Experimental Results from JSOG and Hybrid JSOG**

SOG Type	Pressure (Torr)	Velocity (m/s)	$m_l/m_{Cl}$	P [H <sub>2</sub> O] (Torr)	Y <sub>o</sub> (%)	$\eta_{Cl}$ (%)	Transport Time (ms)
VNIEF	40	40	100	4.6	45	97	~20
SAMARA	30	20	300	1.5	46	89	8

Note: Transport time is the O<sub>2</sub>(<sup>l</sup> $\Delta_g$ ) travel time between the exit of SOG and O<sub>2</sub>(<sup>l</sup> $\Delta_g$ ) detector.

In summary, this literature survey indicates that four major types of SOG designs have been developed since 1978. The advantages and potential limitations of these SOG designs, along with corresponding power class and energy flux, are compared in Table 20.

**Table 20. Comparative Summary of Existing and Conceptual SOG Designs**

SOG Reactor Type	Capacity (Flux)	Advantages	Potential Limitations
<b>Gas-Sparger</b>			
A. Chlorine Bubbler	100 W 0.8 W/cm <sup>2</sup>	• simple design	• low chlorine utilization
B. Fixed Porous Pipe	100 W	• increased interfacial area	• clogging of pores
C. Rotary Porous Pipe	100 W	• increased interfacial area	• clogging of pores
<b>Wetted-Wall</b>			
A. Falling-Film		• simple design	• gravity limited
B. Roller-Drum		• increased interfacial area • adjustable speed	• high recirculation • heat removal
C. Rotating Disk	35 kW 200 W/cm <sup>2</sup>	• increased interfacial area • adjustable speed	• high recirculation • heat removal rate
<b>Jet</b>			
Liquid Jets into Gas	20 kW 400 W/cm <sup>2</sup>	• high yield • easy to model	• costly to fabricate • high recirculation
<b>Atomizer</b>			
A. Gas-Motivated	100 W	• high interfacial area	• high water evaporation • gas-liquid separation
B. Aerosol	30 kW 1.5 kW/cm <sup>2</sup>	• high interfacial area • high energy flux	• high water evaporation • gas-liquid separation

Although the different methods are employed to create surfaces in the form of bubbles, droplets, jets, or films for the chlorine-BHP reaction, all of the existing SOG designs share a common approach as illustrated in Figure 42. This approach follows the steps of (1) generating the liquid (BHP) surface; (2) contacting gaseous chlorine with liquid BHP surface, (3) separating gaseous products from liquid; (4) removing water from the gas phase; (5) removing heat from the liquid phase; and (6) recirculating the liquid BHP. Because all of these SOG designs follow the same basic processing train, typical performance of these SOGs within the ranges of characteristic features (i.e., liquid-phase thickness) does not show any

significant differences as shown in Table 21. Therefore, from the performance viewpoint, the argument whether one SOG design is superior over the rest is subjective and inclusive. Any major advantages would have come from the considerations regarding auxiliary equipment, and logistics to operate and maintain a particular system.

**Table 21. Characteristic Features and Typical Performance of Existing SOGs**

Dimension ( $\mu\text{m}$ )	Gas/Liquid Space Ratio	$A_S/V$ ( $\text{cm}^{-1}$ )	$A_S/V_R$ ( $\text{cm}^{-1}$ )	$Y_{O_2}$ (%)	$U_{Cl_2}$ (%)	Reference
<b>Film Thickness (Rotating-Disk SOG)</b>						
200				65	95	Harpole et al., 1992
350	3.37	28.6	2.8	70	95	Rittenhouse et al., 1999
<b>Jet Diameter (Jet SOG)</b>						
300	66	133	2.0			Zagidullin et al., 1991
500	16	80.0	2.0	60	99	Spalek et al., 1996
700	73	57.1	1.0	85	95	Blayvas et al., 1996
600	114	66.7	0.76	65	85	Furman et al., 1998
<b>Droplet Diameter (Aerosol SOG)</b>						
50	56	1200	582	60	80	Blauer et al., 1987
400	51	150	6.4	60	99	Thayer III, 1992

## 5. Predication of SOG Performance

The changes of concentrations of various reactant and product species, as shown in Figure 3, provide a physical foundation for modeling the chlorine-BHP reaction. As the reaction proceeds, the changes in the concentration of species result in shifting the distribution of reactant and product species. As shown in Figure 4, the rate of singlet oxygen generation is affected by the decrease in the concentration of perhydroxyl anions.

The performance of SOG is typically characterized by the chlorine utilization efficiency (the ratio of chlorine reacted to total chlorine input,  $U(t)$ ), the yield of singlet oxygen (the ratio of singlet delta to total oxygen,  $Y(t)$ ), ultimate oxygen pressure, and the concentration of potential contaminants in the chemical exhaust of the generator. The two key parameters are defined as below.

$$U(t) = [C_1^g(0) - C_1^g(t)]/C_1^g(0) \quad (34)$$

$$Y(t) = C_3^{g0}(t)/[C_1^g(0) - C_1^g(t)] \quad (35)$$

Eqs (34) and (35) lead to the following relationship between the  $O_2(^1\Delta_g)$  yield and chlorine utilization efficiency.

$$Y(t) = [C_3^g(t)/C_1^g(0)]U(t) \quad (36)$$

Furthermore, the efficiency of converting initial chlorine molecules to  $O_2(^1\Delta_g)$  molecules is given by

$$\eta_r = U(t)Y(t) \quad (37)$$

Predictive models have been developed to correlate these two parameters, respectively, with chemical and physical properties of the reaction species. Derivation and application of some of the typical model expressions are discussed below.

### $O_2(^1\Delta_g)$ Yield

A correlation of singlet delta oxygen yield was reported in the early work by Zagidullin et al. (1983). The local yield of singlet oxygen is given by

$$Y = [O_2(^1\Delta_g)]/[O_2] = \{1 + (D_{Cl_2}/\tau_\Delta k [HO_2] D_{O_2})^{1/2}\}^{-1} \quad (38)$$

where  $\tau_\Delta$  is the lifetime of  $O_2(^1\Delta_g)$  in the BHP solution ( $= 2 \mu s$ ),  $k$  is the reaction rate constant ( $= 10^{-8} \text{ L/gmole-s}$ ), and other parameters are as previously defined. Eq (38) holds true for any actual operating conditions of the SOG.

Harpole et al. (1992) developed models for SOG performance based on the rate of change of singlet delta fraction,  $F_\Delta$ , as a function of downstream position,  $z$ ,

$$1/F_{\Delta} = b + 1/F_{\Delta,0} \quad (39)$$

where  $b = 2k_{d1}V_gP^2x_{O_2}/m(RT)^2$ , and  $F_{\Delta,0}$  is the singlet delta fraction at  $z = 0$ . A graphical presentation of this model comparing experimental data is shown in Figure 43. The extrapolation of  $b$  to zero gives the nascent singlet delta fraction.

Harpole et al. (1992) stated that the best performance is with small  $b$ . However, large  $b$  data (low flow rate and/or high pressure) is also useful to identify deactivation mechanisms and reaction rates. The data in Figure 43 indicate a nascent singlet delta fraction of about 80%. The data are consistent with the  $k_{d1} = 1.63 \times 10^4 \text{ m}^3/\text{kmol s}$  reaction rate and singlet sigma deactivating to ground state oxygen. Harpole et al. also stated that surface deactivation of singlet delta oxygen would correlate with pressure over flow rate (as opposed to pressure squared over flow rate in the  $b$  parameter). No correlation of this form was found to further reduce data scatter. Surface deactivation was not significant compared to gas phase deactivation in these tests.

### Chlorine Utilization Efficiency

Zagidullin et al. (1982) developed the following equation to describe the distribution of chlorine along the reaction path of an aerosol-type SOG.

$$[Cl_2(z)] = [Cl_2(z)]_0 \exp(-z/z_{abs}), \quad (40)$$

where  $z_{abs} = u_{mix}/\pi r^2 v \gamma n$ , is the characteristic gas absorption length,  $u_{mix}$  is the velocity of the gas-liquid mixture in the reaction chamber,  $r$  is the radius of the aerosol droplets,  $v$  is the average thermal velocity of molecules,  $\gamma$  is the probability of the chlorine molecule being captured on the surface of a droplet ( $<10^{-2}$ ), and  $n$  is the droplet concentration ( $nr \ll 1$ ). The specific gas-liquid contact surface area is  $4\pi r^2 n$ .

McDermott (1992) presented chlorine utilization efficiency models based on the following mass-transfer model established through the continuity relation in terms of interfacial partial pressure.

$$y = y_0 \exp[(-k_c P / mH) a V_g], \quad (41)$$

where  $y_0$  and  $y$  are the mole fractions of chlorine in the gas phase at the gas-liquid interface at the onset of the SOG and a location downstream, respectively;  $k_c$  is mass transfer coefficient (cm/s);  $P$  is the total pressure at the gas-liquid interface (kPa);  $H$  is Henry's law constant ( $\text{cm}^3 \text{ kPa/mole}$ );  $m$  is total molar gas flow rate (g mole/s);  $a$  is the gas-liquid contact area per unit volume ( $\text{cm}^{-1}$ ); and  $V_g$  is total gas volume of the reactor ( $\text{cm}^3$ ). For an SOG operated at constant pressure and reaction rate-limited conditions, eq(49) can be rearranged into the following form:

$$y = y_0 \exp[(-k_c / mH) (a V_g / F)], \quad (42)$$

where  $m_H$  is the reduced Henry's Law constant ( $= H/RT$ ); and  $F$  is the volumetric flow rate ( $= mRT/P$ ). This model consists of several terms which have physical meanings, such as, reactor residence time,  $V_g/F$ ; reaction velocity or liquid phase resistance,  $k_c/m_H$ ; SOG performance parameter,  $a$ ; and chlorine absorption rate per unit surface area  $k_c/(m_H F)$ . This model is practically expressed in the form of functional dependence of the chlorine utilization efficiency,  $\eta_c (= 1 - y/y_0)$ . Specific model expressions for four limiting cases are summarized in Table 22.

**Table 22. Summary of Mass Transport Models for Predicting SOG Performance**

Reaction Condition	Mass Transport Model
Low Gas Phase Resistance Finite Reaction Rate	$\ln(1-\eta_c) = (-k_c/m_H) (aV_g/F)$ where $k_c = (k c_{HO_2}^0 D_{Cl_2})^{1/2}$
Finite Gas Phase Resistance	$\ln(1-\eta_c) = -K_c (aV_g/F)$ where $1/K_c = m_H/k_c + 1/k_G$ and $k_G = Nu D_g/D_h$
Finite Reaction Rate Unstirred Solution (diffusion rate limited)	$\eta_c = k_L^0 (aV_g/F)$ where $k_L^0 = (2c_{O_2H}^0/c_{Cl_2,g}^0)(D_{O_2H}/\pi t_{exp})^{1/2}$
Infinite Reaction Rate with Gas Phase Diffusion	$\eta_c = 1 - \exp[-(k_G/3) (aV_g/F)]/3$ if $k_L^0 aV_g/F > 1$

The chlorine utilization efficiency model developed by Thayer III (1992) for uniform droplet (aerosol) SOG is given below.

$$U_{Cl_2} = \exp(-C_S/R_T) \quad (43)$$

where  $C_S = \varepsilon L_T/u_g$ ,  $L_T$  is the generator length,  $u_g$  is the mean gas velocity, and  $R_T$  is the transport/reaction resistance for chlorine further defined as

$$R_T = 1/D_1^g + 4/\gamma_{Cl}v_{Cl} + K_d/3(D_1 k[HO_2^-])^{1/2} \quad (44)$$

where  $\gamma_{Cl}$  is sticking probability or sticking coefficient - the fraction of molecular collisions with the droplet surface which results in absorption of a chlorine molecule,  $v_{Cl}$  is the mean chlorine molecular velocity, and  $K_d$  relates the liquid phase/gas phase partial pressure equilibrium.

Similarly, Thayer III (1992) developed a model to calculate singlet oxygen production for uniform droplet SOG.

$$[O_2(^1\Delta_g)]/y_0 = [R' R_{O_2}/(R_T - R_{O_2})][\exp(-C_S/R_T) - \exp(-C_S/R_{O_2})] \quad (45)$$

where  $R' = D_3^g/(D_3^g + \gamma_{O_2}v_{O_2}/4)$ , and  $R_{O_2}$  is the transport/reaction resistance for  $O_2(^1\Delta_g)$  defined as

$$R_{O_2} = 1/D_3^g + 4/\gamma_{O_2}v_{O_2} \quad (46)$$

where  $\gamma_{O_2}$  is the probability of sticking or quenching due to  $O_2(^1\Delta_g)$  collisions with a droplet surface, and  $v_{O_2}$  is the mean oxygen molecular velocity.

### Universal Solution

Copeland and co-workers developed comprehensive mathematical models to predict SOG performance (Copeland et al., 1992; Copeland and Bauer, 1994). These models are represented by three nonlinear, coupled equations given below.

$$\begin{aligned}
 S \frac{dC_1^g}{dt} &= -u_1^e C_1^g \\
 C_1^g(0) &= C_1^{g0} \\
 S \frac{dC_3^g}{dt} &= +Y_S u_1^e C_1^g - u_3^e C_3^g - 2Sk_6 (C_3^g)^2 \\
 C_3^g(0) &= 0 \\
 C_2(t) &= C_2^0 - \int_0^t dt \, 2u_1^e (C_2(\tau)) C_1^g(\tau) \sqrt{\frac{r}{\pi D_2(t-\tau)}}
 \end{aligned}$$

$$\begin{aligned}
 \frac{1}{u_1^e} &= \frac{2H}{D_1^g Sh_1} + \frac{1}{\frac{1}{4} v_1 \gamma_1} + \frac{h_1}{(D_1 k_1 C_2)^{1/2}} \\
 \frac{1}{u_3^e} &= \frac{2H}{D_3^g Sh_3} + \frac{1}{\frac{1}{4} v_3 \gamma_3} + \frac{h_3}{(D_3 k_4)^{1/2}} \\
 Y_S &= \frac{1}{(1+\phi_2)(1+\phi_3+\phi_4)} \\
 \phi_2 &= \left( \frac{D_1 k_4}{D_3 k_1 C_2} \right)^{1/2} \\
 \phi_3 &= \frac{(D_3 k_4)^{1/2}}{\frac{1}{4} v_3 \gamma_3 h_3} \\
 \phi_4 &= \frac{(D_3 k_4)^{1/2}}{h_3} \frac{2H}{D_3^g Sh_3}
 \end{aligned}$$

where

A semi-analytical solution of these equations was developed to describe the chlorine consumption and  $O_2(^1\Delta_g)$  formation processes based on the chlorine-BHP reaction. Key parameters used in these models are summarized in Table 23.

**Table 23. Parameters Governing the  $O_2(^1\Delta_g)$  Generator Solution**

Parameter	Expression	Value	Implication
$\tau_1$	$S_v/u_1^{GI}$	1 – 10 ms	$Cl_2$ gas-phase lifetime
$\alpha$	$2k_6 C_1^{g0} S/u_1^{GI}$	0.015 – 1.5	$O_2(^1\Delta_g)$ gas-phase pooling losses
$\beta$	$u_1^{GI}/u_1^{R0}$	0.1 – 1.0	Effect of the finite $Cl_2/HO_2$ reaction rate on the $Cl_2$ mass transfer coefficient
$\gamma$	$(ru_1^{GI} S/\pi D_2 M^2)^{1/2}$	0.1 – 20	“Freshness” of the $HO_2$ surface concentration
$\delta$	$(D_1 k_4/D_3 k_1 C_2^0)^{1/2}$	0.1 – 0.2	Probability of $O_2(^1\Delta_g)$ deactivation relative to $O_2(^1\Delta_g)$ formation in the liquid
$Y_S^0$	$[(1+\delta)(1+\phi_3+\phi_4)]^{-1}$	0.8 – 0.9	Probability of an $O_2(^1\Delta_g)$ formed in the liquid will escape to the bulk gas phase

Note:  $S_v$  - ratio of gas volume to liquid surface area (cm),  $C$  (concentration),  $D$  (diffusion coefficient),  $u$  (mass transport coefficient),  $Sh$  (Sherwood number),  $H$  (dimensionless Henry's

constant),  $v$  (velocity in the gas-liquid interface), and  $\gamma$  (probability that a component sticks to the liquid BHP), the subscripts 1, 2, and 3 denotes  $\text{Cl}_2$ ,  $\text{HO}_2$  and  $\text{O}_2(^1\Delta_g)$ , respectively. The superscript  $g$  denotes a gas phase value while the absent of such a superscript denotes a liquid phase value. The superscript 0 denotes the initial value of the variable, i.e., its value at  $t = 0$ , while a subscript 0 denotes the value of the variable at the gas-liquid interface, i.e.,  $x = 0$ .

### Thermal Analysis

The heat ( $q$ ) generated in the SOG is given by the product of the chlorine flow rate ( $m_c$ ), chlorine utilization efficiency ( $U$ ), and the effective heat of reaction ( $Q_r$ ).

$$q = m_c U Q_r \quad (50)$$

$Q_r$  includes effects of nonideal yield, thermal energy carried by the gas phase, and water evaporation.

Dickerson et al. (1992) developed the following bulk temperature rise model for rotating-disk SOG.

$$T_b = T_0 + q \{t - t_m [1 - \exp(-t/t_m)]\} / (M_m C_{pm} + M_b C_{pb}) \quad (51)$$

$$T_m - T_b = q t_m [1 - \exp(-t/t_m)] / M_m C_{pm} \quad (52)$$

where  $T_b$  is the BHP bath temperature,  $T_0$  is the initial BHP temperature,  $T_m$  is the mixture temperature intermediate between the average film temperature ( $T_f$ ) and  $T_b$ ,  $M_m$  is the equivalent mass of bulk BHP + generator,  $M_b$  is the equivalent mass of disks + BHP,  $C_{pm}$  and  $C_{pb}$  are heat capacity of the equivalent mass, and  $1/t_m = m_c C_p / M_m C_{pm} + m_c C_p / M_b C_{pb}$ . The value for  $Q_r$  (cal/mol  $\text{Cl}_2$ ) is given by the following equation.

$$Q_r = 26,100 + 22,530 (1 - Y) \quad (53)$$

In the example provided by Dickerson et al. (1992), a value of 0.45 was used for  $Y$ , and the calculated  $Q_r$  was 38,492 cal/mol  $\text{Cl}_2$ .

The film skin temperature rise is given by the following equations.

$$T = T_m + \Delta T - \Delta T \operatorname{erf}[z / (4kt / \rho C_{pl})^{0.5}] \quad (54)$$

and

$$\Delta T = Q_r [\text{HO}_2^-]_0 (D_{\text{HO}_2^-} / 4k\rho C_{pl})^{0.5} \quad (55)$$

where  $T$  is the film skin temperature,  $z$  is the depth beneath the surface of the liquid,  $k$  is the rate of chlorine-BHP reaction,  $t$  is time,  $\rho$  is density of liquid BHP, and  $C_{pl}$  is the heat capacity of liquid BHP.

### Simplified Kinetic Model

Perram (1994) reported results from a detailed, computational study on the gas phase kinetics associated with COIL devices. Based on a standardized kinetic package developed in the study, simplified kinetic models are reported to assess kinetic limitations to COIL performance. A total of 48 kinetic processes are recommended to describe the COIL process (see Appendix B). Eleven of these reactions are considered to be critical (i.e., kinetic sensitivity  $S = 1$ ) to any COIL kinetic model. These eleven reactions and rate coefficients are given in Table 24 (Perram, 1994). In these reactions,  $I^*$  denotes the upper laser level,  $I(^2P_{1/2})$ , and  $I_2^*$  denotes vibrationally excited molecular iodine ( $I_2$ ). Of these 48 and 11 kinetic processes for COIL devices, 13 and 2 reactions are specific to the SOG operation, respectively.

Based on these 11 reactions, five independent differential equations are obtained by transforming to eleven non-dimensional variables. Since there are no iodine species involved in an SOG system, the kinetic model developed by Perram (1994) for COIL devices can be simplified as follows.

$$\ln(\alpha) = AT + 1 - \exp(AT) \quad (56)$$

where

$$\alpha = [O_2(^1\Delta_g)]/[O_2(^1\Delta_g)]_{t=0}$$

$$A = r_3/(r_2W) + 2r_4$$

$$T = t(k_1 + 2k_3) [O_2(^1\Delta_g)]_{t=0}$$

$$W = [H_2O]/[H_2O]_{t=0}$$

$$r_i = k_i/\{2(k_1 + 2k_3)\}$$

$t$  = time

Table 24. Rate Coefficients for Simplified COIL Reaction Mechanism (Perram, 1994)

Rxn	Kinetic Process	$k_i$	S
1	$O_2(a^1\Delta) + O_2(a^1\Delta) \rightarrow O_2(b^1\Sigma) + O_2(X^3\Sigma)$	$2.7 \times 10^{-17}$	1
5	$O_2(b^1\Sigma) + H_2O \rightarrow O_2(a^1\Delta) + H_2O$	$6.7 \times 10^{-12}$	1
21	$I_2(X^1\Sigma) + O_2(b^1\Sigma) \rightarrow I + I + O_2(X^3\Sigma)$	$4.0 \times 10^{-12}$	1
32	$I_2(X^1\Sigma) + O_2(a^1\Delta) \rightarrow I_2^* + O_2(X^3\Sigma)$	$7.0 \times 10^{-15}$	1
33	$I_2(X^1\Sigma) + I^* \rightarrow I_2^* + I$	$3.8 \times 10^{-11}$	1
34	$I_2^* + O_2(a^1\Delta) \rightarrow I + I + O_2(X^3\Sigma)$	$3.0 \times 10^{-10}$	1
36	$I_2^* + H_2O \rightarrow I_2(X^1\Sigma) + H_2O$	$3.0 \times 10^{-10}$	1
40	$I + O_2(a^1\Delta) \rightarrow I^* + O_2(X^3\Sigma)$	$7.8 \times 10^{-11}$	1
41	$I^* + O_2(X^3\Sigma) \rightarrow I + O_2(a^1\Delta)$	$2.7 \times 10^{-11}$	1
44	$I^* + O_2(a^1\Delta) \rightarrow I + O_2(b^1\Sigma)$	$1.1 \times 10^{-13}$	1
48	$I^* + H_2O \rightarrow I + H_2O$	$2.0 \times 10^{-12}$	1

Simplified Reaction Mechanism  
(Rate Coefficients in  $\text{cm}^3/\text{molecule}\cdot\text{s}$ )

## 6. Design Improvement Aspects

To create a new generation of SOG that is technologically superior over the four major types of SOG already developed, one must address the basic requirements of the COIL process described in the previous sections. Based on the published information about the merits and limitations of each type of SOG designs, a number of design considerations have been suggested to enhance the yield of singlet oxygen generation and energy flux. Integration of SOG with downstream system components, such as iodine mixing nozzle, is also an important aspect for SOG design improvement. Since one of the key issues is thermal management, any improved method developed for SOG may be directly applicable to other related processes such as production of BHP and neutralization of spent BHP. It is also desirable to develop a multi-purpose device that can be used for BHP production and neutralization processes as well as singlet oxygen generation. Four important SOG design aspects that require further improvement are briefly described below.

### Water Minimization and Removal

The importance of water vapor control is best illustrated by plotting the COIL power output as a function of water mole fraction as shown in Figure 44 (Truesdell et al., 1994). The normalized COIL power output linearly decreases with increasing water vapor. For each fold of increase in water vapor mole fraction, the normalized COIL power output reduces about 15%. This is the result of a combined effect of water on singlet oxygen and iodine chemistry.

Therefore, the control and removal of water vapor content in the product stream have been a focus point and challenge for SOG development. The water vapor content in an SOG is contributed from the following two sources:

- the bulk water introduced by MHP (typically 50% by weight of MHP); and
- the product water generated from the chlorine-MHP reaction (the stoichiometric ratio of water to singlet oxygen is 2 to 1).

Although the amount of water from the chlorine-MHP reaction is relatively small compared to the bulk water in MHP, the former is produced at the gas-liquid interface and is more likely to escape to the vapor phase.

Traditionally, two approaches have been used: (1) vapor cold traps to condense water and (2) lowering MHP bath temperature to prevent water vapor formation. Both of these approaches have their limitations.

### Injection Nozzle Design

The nozzle is one of the most critical components of any given SOG because it is used to generate gas-liquid interface for the chlorine-BHP reaction. There are several basic types of nozzle arrangements including (1) liquid BHP as the primary fluid and gaseous chlorine as the secondary fluid; (2) gaseous chlorine as the primary fluid and liquid BHP as the secondary

fluid; and (3) chlorine and BHP having independent injection ports. If the nozzle openings are small, as in the case of jet-SOG and aerosol-SOG, the solids in a BHP may become an operational problem. Therefore, there is a need to develop solids-tolerant nozzles for jet and aerosol SOG's. The key factors in nozzle designs are to rapidly create new surfaces between the gas and liquid streams, and at the same time to minimize the contact time and to rapidly separate the singlet oxygen from the reactor effluent.

### **Total Pressure**

Major benefits from operating an SOG at high pressures include the intensification of energy flux and reduce auxiliary equipment for transporting and discharging the reactor effluent to ambient environment. However, one of the major limitations in the existing SOGs is that both the yield of singlet oxygen production and chlorine utilization efficiency are inversely proportional to the operating pressure. Pressures up to 300 torr have been reported in some SOG studies. At this pressure, the singlet oxygen yield is about 20% lower than that obtainable at lower pressures typically around 20 torr. The decrease in chlorine utilization efficiency is more sensitive to the gas pressure rise. Raising the operating pressure while keeping both the singlet oxygen yield and chlorine utilization efficiency sufficiently high will be a major challenge in the new SOG designs.

### **Heat Transfer Options**

Another area of interest is to improve heat removal efficiency and thermal energy management for SOG operation. This improvement would translate to more compact SOG systems. Three approaches may be considered to improve thermal energy management:

- utilizing the heat of vaporization of the feed streams (chlorine and diluent) to dissipate in part the heat of SOG reaction since these feed streams are stored in the liquid state;
- improving heat exchanger hardware efficiency; and
- exploring different heat exchange methodologies (i.e., direct contact vs. conventional indirect heat transfer options).

## 7. Other Related Issues

### SOG Modeling and Simulation

Computational Fluid Dynamics (CFD) has become a powerful and practical tool for process simulation in the chemical industries. This technique has been applied to studying COIL as the result of current interest and ongoing commercial and military development programs. Accurate models of the gas dynamics and chemistry involved in various components of a COIL have recently been developed using CFD codes (Madden et al., 1999; Yang et al., 2000). Much of the effort has focused on simulating the performance of supersonic iodine injection nozzles. However, the CFD tool can be equally beneficial for assisting the development of new SOG's.

### SOG Diagnostics

It is also recognized that the ability of detecting and quantifying singlet oxygen is one of the basic requirements for studying and improving SOG designs. Parallel to the R&D effort in COIL, a number of  $O_2(^1\Delta_g)$  detection techniques have been developed and used in the reported SOG studies. Table 25 summarizes basic diagnostic techniques that have been reported in the literature for the measurement of gaseous (i.e.,  $O_2(^1\Delta_g)$ ,  $Cl_2$ ,  $H_2O$ , and  $O_2$ ) and liquid (i.e.,  $OH$ ,  $H_2O_2$ ) species. Detailed discussion on the subject of analytical techniques is beyond the scope of this literature review.

**Table 25. Basic Requirements and Techniques for SOG Diagnostics**

Species	Typical Concentration*	Detection Technique	Reference
$O_2(^1\Delta_g)$	5 – 10%	EPR spectroscopy Ratiometric Wang Detector Diode Laser Piston Source Method	Benard and Pchelkin, 1978  Keating et al., 2000 Duo et al., 2000
Water Vapor	0 – 8%	Quadrupole Mass-Spec Diode Laser  CRDS	Bunn and Tomassian, 1994 Davis et al., 1998, Kendrick et al., 1998, Furman et al., 1999 Sun et al., 1998
Chlorine	0 – 8%	Quadrupole Mass-Spec Absorption at 350 nm	Bunn and Tomassian, 1994 Furman et al., 1999
Total Oxygen	15 – 30%	Quadrupole Mass-Spec Diode Laser Diode Laser	Bunn and Tomassian, 1994 Davis et al., 1998 Furman et al., 1999
Total Base	4 – 8 mole/kg	Titration	Dinges et al., 1994
Hydrogen Peroxide	4 – 8 mole/kg	Titration	Dinges et al., 1994

\* Balance in the gaseous stream is the diluent, typically  $H_e$ .

## BHP Regeneration for COIL Applications

For large-scale, continuous operation of COIL, the regeneration and/or disposal of BHP become(s) extremely important. Demyanovich and Lynn (1986) of TERA Corporation (Berkeley, CA) reported a detailed process design and evaluation of a continuous chemical plant for COIL. The study focused on using the Chlor-Alkali Process to electrolytically regenerate chlorine and sodium hydroxide from the spent BHP. Hydrogen generated from the Chlor-Alkali Process is further utilized in the Anthraquinone Process to produce hydrogen peroxide. The analysis shows that the overall energy efficiency of singlet oxygen production, the ratio of the energy of the singlet oxygen produced to the energy required for singlet oxygen production, is 3.6% for stoichiometric process and 3.3% for nonstoichiometric (i.e., excess hydrogen peroxide) process.

Dinges et al. (1994) at Applied Laser Technology Branch, U.S. Air Force Phillips Laboratory (Kirtland AFB, NM) studied the regeneration of BHP by chemical additions to the spent BHP. Potassium superoxide was used and compared with the conventional method of adding concentrated hydrogen peroxide (70%) and KOH solid. The BHP cycle is shown in Figure 45. The results show that either of the regeneration methods can be used to restore the  $O_2H$  molarity, but the use of standard reagents is recommended primarily based on the costs of the reagents.

There are two key issues need to be addressed to achieve long-term operation of COIL. As discussed earlier (see Figure 10), the first issue is the formation of solid salts. The second issue is the reduction of base concentration, which increases the BHP freezing point and decreases the laser power output. Naito et al. (1997) presented a BHP recycling system, which was designed and tested in conjunction with a 10-kW class COIL. As shown in Figure 46, the process involves (1) filtering salt from the spent BHP, (2) removing water by evaporation and vapor trap, and (3) adding hydrogen peroxide and KOH solutions.

Vetrovec (1997) proposed the concept for continuous in situ regeneration of BHP and chlorine by electrolytic cells. The concept combines the conventional membrane-type chlor-alkali process with the basic hydrogen peroxide process developed by Dow Chemical Company. The configuration of the proposed regeneration loop by Vetrovec is shown in Figure 47. The Dow's BHP process was developed for use in the pulp and paper industry in the 1980's. The efficiency of the BHP regeneration process is governed by the performance of the peroxide cell in terms of peroxide concentration and the peroxide-to-base (P/B) concentration ratio. The Dow's process typically produces a P/B molar ratio of 0.6:1, which is less than the required P/B molar ratio of 1:1, and preferably 1.1:1 for COIL applications. Vetrovec (1997) predicted the current efficiency of the regeneration process to be about 50%, which translates to 3 – 4% wall plug efficiency for the COIL laser. Missile Defense Agency (MDA) recently issued a request for proposal to develop electrochemical chemical oxygen iodine laser (EC COIL) fuels regeneration system (FRS) (Broad Agency Announcement AL2003-01, Technical Area 5). The primary goal of this technology development effort is to demonstrate a fuels regeneration system for sustained operation of COIL devices. The FRS will consist of an exhaust gas capture and separation subsystem/gas processing subsystem (GPS), liquids processing subsystem (LPS), and a reagent production subsystem (RPS) to

produce the principle fuels from the laser waste products. This recent call for technology development indicates that the need for material management in COIL operations is real and urgent particularly for reduction of logistic support requirements in military applications.

### Material and Equipment Requirements for Industrial COIL

Early attempts on developing industrial applications of COIL were made by Japanese researchers (Fujii et al., 1990; Naito et al., 1997; Endo et al., 1998). Cutting performance of COIL was also reported (Latham et al., 1998). According to Zagidullin and Nikolaev (1999), the biggest challenge for the development of high power supersonic industrial COIL is the requirement of a high capacity vacuum pump station. Other issues to be addressed for practical applications of COIL include the use of nitrogen as the diluent in place of helium, chemical recycling, and waste management. An example of a large-scale, open cycle COIL operation based on the Verti-JetSOG design is presented below (Zagidullin and Nikolaev, 1999). A simplified process scheme for the COIL operation is shown in Figure 48. Table 26 provides projected operational parameters and conditions of required hardware for an 8-hour operation of 10-kW COIL (288 MJ total energy). It is assumed that the chemical efficiency is 30% and the reduction of BHP concentration from 8 M to 4 M KOH has no effect on the power output. It is also projected that the singlet oxygen yield is above 70% and chlorine utilization efficiency is above 90%.

**Table 26. Projected Parameters and Conditions for Operating a 10-kW COIL**

Cl <sub>2</sub> flow rate	0.37 mole/s	Jet SOG and plenum pressure	50 Torr
Primary N <sub>2</sub> flow rate (80K)	0.74 mole/s	Mach number in laser cavity	0.7
Secondary N <sub>2</sub> flow rate	0.37 mole/s	Estimated small signal gain	2% cm <sup>-1</sup>
Iodine flow rate	3.7 mmole/s	Pump rate at 20 Torr	1.4 m <sup>3</sup> /s
BHP flow rate	5 L/s	Total BHP weight	7700 kg
Pressure in laser cavity	20 Torr	Total BHP volume	5.3 m <sup>3</sup>
Heat exchanger cooling power	47 kW	Total LN2 weight	~ 1000 kg

## 8. Summary

The principle and chemistry for COIL based on the chlorine-BHP reaction have been well established since the inception of the COIL concept in late 1970's. Currently, major challenges to develop COIL devices for military and industrial applications stem from efficient and compact designs of system hardware such as SOGs and closed-loop material management. For ABL applications, process safety and logistics associated with in-flight operations pose additional challenges. Among the major components of a COIL device, SOG plays one of the most critical roles in determining the chemical efficiency of the COIL system, since the energy loss in a typical SOG operation accounts to as much as 40% of the total energy losses in the COIL system.

The SOG development has evolved into four basic types of SOG designs: (1) gas-sparger; (2) wetted-wall; (3) jet, and (4) atomizer. Among these designs, the rotating-disk SOG's (wetted-wall type) and jet-SOG's have received most attention and produced the largest laser output to date ( $10^1$  to  $10^2$  kW). The yield of  $O_2(^1\Delta_g)$  production obtained from these reported SOGs typically ranges from about 20% for the gas-sparger SOG to about 90% for the Jet SOG. The chlorine utilization efficiency typically ranges from 95% to 99%. Recently, hybrid SOG designs combining features from the four basic designs have been reported. Improved results have been obtained on a twisted-flow aerosol SOG based on the aerosol design concept while incorporating some of the Jet SOG features. Various predictive models for the  $O_2(^1\Delta_g)$  yield and chlorine utilization efficiency have been formulated and validated. Thermal analysis and kinetic models for SOG operations are also available.

An increasing amount of engineering design data, hardware, and applications for COIL and its components has become available in the open literature. However, further R&D is still needed in the areas of novel SOG designs, system integration, process scale-up, and chemical handling to improve the chemical efficiency and sustainability of the COIL process. Desirable features for new SOG designs may include water minimization/removal, improved injection nozzles, high-pressure system, and heat transfer enhancement. The state-of-the-art CFD simulation can be a useful tool to assist experimental studies on the existing and conceptual SOG designs. This continued R&D effort may potentially benefit the development of a multi-purpose device that can be used for singlet oxygen generation, BHP production, and spent BHP neutralization.

## 9. Appendices

### Appendix A: Gas-Liquid Reactions

#### Characterizations of Gas-Liquid Reactions

From the modeling viewpoint, the chlorine-BHP reaction can be considered as a gas-liquid diffusional mass-transfer accompanied by a fast, irreversible chemical reaction. Assuming that the bulk fluid density,  $\rho$  ( $\text{g}/\text{cm}^3$ ), is constant, the process is governed by the Fick's law of diffusion,

$$j_{Ay} = -\rho D_{AB} d/dy(\omega_A) \quad (\text{A-1})$$

where  $j_{Ay}$  is the flux of species A in the y direction ( $\text{g}/\text{cm}^2 \text{ s}$ ),  $D_{AB}$  is the diffusivity of species A in species B ( $\text{cm}^2/\text{s}$ ), and  $\omega_A$  is the mass fraction of species A. Similarly, the Fick's law of diffusion can be expressed on the molar basis,

$$N_A - x_A(N_A + N_B) = -c D_{AB} \nabla x_A \quad (\text{A-2})$$

where  $N_A$  and  $N_B$  (vectors) are the flux of species A and B, respectively ( $\text{gmole}/\text{cm}^2 \text{ s}$ ),  $c$  is the total molar concentration ( $\text{gmole}/\text{cm}^3$ ), and  $x_A$  is the mole fraction of species A.

A practical form of the above equations is commonly used to describe the mass transfer rate in a gas-liquid contactor (Charpentier, 1981),

$$\Phi = \varphi a = k_G a (p - p_i) = k_L a (C_A^* - C_{A0}) \quad (\text{A-3})$$

where  $\Phi$  is the rate of gas absorption per unit volume of reactor ( $\text{gmole}/\text{cm}^3 \text{ s}$ ),  $\varphi$  is the average rate of absorption per unit interfacial area ( $\text{gmole}/\text{cm}^2 \text{ s}$ ),  $a$  is the gas-liquid interfacial area per unit volume ( $\text{cm}^2/\text{cm}^3$ ),  $p$  and  $p_i$  are the partial pressures (bar) of soluble gas in the bulk gas and at the interface,  $C_A^*$  is the concentration ( $\text{gmole}/\text{cm}^3$ ) of dissolved gas corresponding to equilibrium with  $p_i$ , and  $C_{A0}$  is the average concentration ( $\text{gmole}/\text{cm}^3$ ) of dissolved gas in the bulk liquid.  $k_G$  and  $k_L$  are the gas-side and liquid-side mass transfer coefficient ( $\text{cm}/\text{s}$ ), respectively.

The overall mass transfer coefficient is related to the liquid-side mass transfer coefficient  $k_L$  and the gas-side mass transfer coefficient  $k_G$  through the Henry's law constant  $H$  ( $\text{atm cm}^3/\text{gmole}$ ) by the following equation.

$$1/K_L = 1/k_L + 1/Hk_G \quad (\text{A-4})$$

Since  $a$  in eq (A-3) is difficult to quantify, the term  $k_L a$  ( $1/\text{s}$ ) - volumetric mass transfer coefficient, is often used as one of the key parameters for describing gas-liquid reactions. For example,  $k_L a$  typically shows a linear relationship with volumetric flow rate of the gas,

$$k_L a = c_1 + c_2 Q_G \quad (\text{A-5})$$

where  $c_1$  and  $c_2$  are constants and  $Q_G$  is the volumetric flow rate of the gas ( $\text{cm}^3/\text{s}$ ) (Prasad and Ramanujam, 1995; Billerbeck et al., 1999).

The chlorine-BHP reaction in COIL systems can be best described by a dissolved gas (component A - chlorine) undergoes an irreversible second-order reaction with a reactant (component B - perhydroxyl anion) dissolved in the liquid given as,  $A + zB \rightarrow \text{products}$ , with the rate equation,  $r_A = k_2 C_A C_B$ . The presence of a chemical reaction in the liquid, depending on the intensity of the chemical reaction, may enhance mass transfer. The ratio of the volumetric mass transfer coefficient  $(k_L a)_{\text{chem}}$  in the presence of a chemical reaction to the volumetric mass transfer coefficient  $(k_L a)_{\text{phys}}$  without a chemical reaction is defined as the enhancement factor,  $E$ ,

$$E = (k_L a)_{\text{chem}} / (k_L a)_{\text{phys}} \quad (\text{A-6})$$

The enhancement factor  $E$  can be plotted, Figure A-1, as a function of the dimensionless parameter, Hatta number,

$$\text{Ha} = (D_A k_2 C_{B0})^{1/2} / k_L \quad (\text{A-7})$$

of the concentration-diffusion parameter  $Z_D$ ,

$$Z_D = (D_B / z D_A) (C_{B0} / C_A^*) \quad (\text{A-8})$$

and of the ratio between the volume of liquid associated with unit interface area and the film thickness parameter  $(\beta/a) (k_L / D_A)$ , where  $\beta$  is liquid holdup and  $D_A$  and  $D_B$  are the molecular diffusivity of component A and B in very dilution solution, respectively. The value of Hatta number provides an important indication of whether a large specific interfacial area  $a$  or large liquid holdup  $\beta$  is required for a particular reaction of rate constant  $k_2$ .

For mass transfer process coupled with instantaneous reaction (i.e.,  $\text{Ha} > 10 E$ ), the reaction occurs completely in the liquid film during the transport of component A. The concentration of A in the bulk liquid is virtually zero. Thus, the average rate of absorption per unit interfacial area can be expressed by the following equation, also known as the Higbie model.

$$\varphi = E k_L C_A^* \quad (\text{A-9})$$

For absorption of a gas having constant partial pressure into a quiescent medium followed by instantaneous reaction,  $E$  can be expressed by the following equation (Danckwerts, 1970),

$$E = (Q / 2 C_A^*) (\pi / D_A \theta)^{1/2} \quad (\text{A-10})$$

where  $Q$  is the amount of absorption per unit interfacial area,  $D_A$  is the liquid diffusivity of the dissolved gas, and  $\theta$  is time after the interfacial concentration of liquid-phase reactant falls to zero.

For mass transfer with significant gas-side resistance, the two-film model should be used. The rate of gas absorption with instantaneous irreversible reaction is given as

$$\Phi = \phi a = [p + (HD_B C_{B0}/zD_A)] / [(k_G a)^{-1} + (H/k_L a)] \quad (\text{A-11})$$

The interface concentration profiles and the corresponding absorption rate forms for mass transfer processes coupled with chemical reactions in eight distinct kinetic regimes are summarized in Figure A-2.

### Reactors for Gas-Liquid Reactions

Gas-liquid reactors, also known as gas-liquid contactors, are encountered in many chemical processes. Gas-liquid contactors may be classified into surface and volume contactors, where the interfacial area between the two phases is created at the liquid surface and within the bulk of liquid, respectively. Another classification is based on level of mass transfer rate. Gas-liquid contactors without internal mechanical energy dissipation have in general low mass-transfer rates and may be called "low performance contactors." The increase in the  $k_L a$ -value due to mechanical energy dissipation may be greater than one order of magnitude. Such gas-liquid contactors are usually called "high performance contactors" (Gaddis, 1999).

Surface gas-liquid contactors may also be divided into two groups: impeller or liquid jet contactors. In the first group, impellers or rotors submerged in the liquid near the surface are used to create the required gas-liquid interfacial area and in the latter it is achieved by means of liquid jets impinging on the liquid surface. A rotating horizontal drum partly submerged in the liquid provided with or without additional extended surfaces is also a surface contactor. The drum brings continuously a thin film of liquid from the bulk into the surface. In a volume gas-liquid contactor, the gas phase is dispersed in the form of small or large bubbles with regular spherical or irregular shape. Gas dispersion in the liquid may be achieved by different methods. The most common methods encountered in gas dispersion are the use of spargers, liquid jets through two-mixture nozzles, or hollow rotating mixers.

The selection of a gas-liquid reactor for a specific application depends on process requirements such as gas/liquid flow, mass transfer, and chemical reaction characteristics. Table A-1 summarizes the liquid holdup (gas-liquid volumetric flow rate ratio), gas-side and liquid-side mass transfer coefficients, and interfacial area for a number of conventional gas-liquid contactors (Carpentier, 1981; Billerbeck et al., 1999). Principal types of laboratory techniques for studying gas-liquid reactions are shown in Figure A-3 (Carpentier, 1981). Typical ranges of  $k_L$ , contact time, and interfacial area for each type of gas-liquid reactors are also given in Figure A-3.

Table A-1. Mass Transfer Performance of Conventional Gas-Liquid Contactors

Type of Reactor	$\beta$ (%, gas-liquid volume)	$k_G$ (gmol/cm <sup>2</sup> s atm)x10 <sup>4</sup>	$k_L$ (cm/s)x10 <sup>2</sup>	$a$ (cm <sup>2</sup> /cm <sup>3</sup> reactor)	$k_L a$ (s <sup>-1</sup> )x10 <sup>2</sup>
Packed columns					
Countercurrent	2 - 25	0.03 - 2	0.4 - 2	0.1 - 3.5	0.04 - 7.0
Cocurrent	2 - 95	0.1 - 3	0.4 - 6	0.1 - 17	0.04 - 102
Plate columns					
Bubble cap	10 - 95	0.5 - 2	1 - 5	1 - 4	1.0 - 20
Sieve plates	10 - 95	0.5 - 6	1 - 20	1 - 2	1.0 - 40
Bubble columns	60 - 98	0.5 - 2	1 - 4	0.5 - 6	0.54 - 24
Packed bubble columns	60 - 98	0.5 - 2	1 - 4	0.5 - 3	0.54 - 12
Tube reactors					
Horizontal and coiled	5 - 95	0.5 - 4	1 - 10	0.5 - 7	0.50 - 70.0
Vertical	5 - 95	0.5 - 8	2 - 5	1 - 20	2.0 - 100
Spray columns	2 - 20	0.5 - 2	0.7 - 1.5	0.1 - 1	0.07 - 1.5
Mechanical agitated					
bubble reactors	20 - 95	-	0.3 - 4	1 - 20	0.30 - 80
Submerged and plunging jet	94 - 99	-	0.15 - 0.5	0.2 - 1.2	0.03 - 0.60
Hydrocyclone	70 - 93	-	10 - 30	0.2 - 0.5	2.0 - 15
Ejector reactor	-	-	-	1 - 20	-
Venturi	5 - 30	2 - 10	5 - 10	1.6 - 25	8.0 - 25
Aero-ejector	5 - 20	-	-	-	1.0 - 12

### Power Requirement

The power input necessary for a given mass transfer performance is an essential characteristic of a gas-liquid contactor. Typically, power is introduced into the system in two forms: the power for gas compression to overcome the pressure drop of the whole system,  $W_G$ , and the hydraulic power,  $W_L$ , necessary for recirculating the liquid through the system. For a gas generated from boiling liquid, the power is governed by the saturation pressure at a given temperature and heat input for evaporation. The hydraulic power is given by

$$W_L = Q_L \Delta P_L \quad (\text{A-12})$$

where  $Q_L$  is the volumetric flow rate of the liquid (cm<sup>3</sup>/s) and  $\Delta P_L$  is the pressure difference between the reactor inlet and outlet.

The increase in free surfaces of a system requires energy. For surface gas-liquid contactors, energy dispersion is accomplished by spray nozzles, which turn a volume of liquid into droplets. For liquids, the energy required to increase its surface can be estimated from the surface tension of a liquid,  $\sigma$ , which is defined as the force per unit length (dyn/cm) on the surface that opposes the expansion of the surface area. The surface tension of water at 0°C

equals to 75.85 dyn/cm (or erg/cm<sup>2</sup>). Based on this value, the value of the relative energy density of water can be estimated at each given surface area per liter of water. These calculated values along with volume, surface area and total droplet count per liter of liquid are given in Table A-2. In practice, the energy required for operating spray nozzles can be in the form of pressure provided by gravity or a pump, or a stream of compressed gas to pull the liquid apart. As the diameter of droplets reduces from 2000 to 15  $\mu\text{m}$ , the total surface area of the droplets generated from a given volume of liquid increases more than 100 times. However, the energy buildup on these surfaces also increases in the same order of magnitude.

**Table A-2. Volume, Surface Area and Energy Density for Droplets of Various Diameters**

Droplet Diameter ( $\mu\text{m}$ )	Surface Area of 1 Droplet ( $\text{mm}^2$ )	Volume of 1 Droplet ( $\text{mm}^3$ )	Total Droplet Count/Liter	Total Surface Area/Liter ( $\text{m}^2$ )	Relative Energy Density (Water) (J/Liter)
2000	12.6	4.19	$2.39 \times 10^5$	3.0	0.228
1000	3.14	$5.24 \times 10^{-1}$	$1.91 \times 10^6$	6.0	0.455
500	0.785	$8.55 \times 10^{-2}$	$1.53 \times 10^7$	12.0	0.910
250	0.196	$8.19 \times 10^{-3}$	$1.22 \times 10^8$	24.0	1.82
125	0.0491	$1.02 \times 10^{-3}$	$9.77 \times 10^8$	48.0	3.64
60	0.0113	$1.13 \times 10^{-4}$	$8.84 \times 10^9$	100	7.59
30	0.00283	$1.41 \times 10^{-5}$	$7.07 \times 10^{10}$	200	15.2
15	0.000707	$1.77 \times 10^{-6}$	$5.65 \times 10^{11}$	400	30.3

## Appendix B: SOG Design Databases

### COIL Energy and Power Calculations

Based on the singlet oxygen production and lasing reactions (eqs 5-8), stoichiometric requirements of the chemical fuels and energy/power potentials for COIL systems are shown in Tables B-1 and B-2, respectively. Examples are given for four different MHP recipes covering a range of MOH concentrations from 4.20 to 5.00 mole/kg MHP. In all of the cases, excess hydrogen peroxide is used. The molar ratio of peroxide to base concentrations is typically 1.15. For each mole of singlet oxygen produced, the stoichiometric requirements for Cl<sub>2</sub> and I<sub>2</sub> are 1:1:0.25. The calculated power output is based on the assumption that the overall COIL chemical efficiency and power extraction efficiency are 25% and 80%, respectively (Rittenhouse et al., 1999).

**Table B-1. Stoichiometric Requirements and Energy Potential per kg MHP**

MHP Recipe	H <sub>2</sub> O <sub>2</sub> (mol/kg)	MOH (mol/kg)	Cl <sub>2</sub> (mol/kg)	O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> ) (mol/kg)	I <sub>2</sub> (mol/kg)	Energy Available	
						(kcal/kg)	(kJ/kg)
420	4.65	4.20	2.10	2.10	0.525	47.3	198
450	5.23	4.50	2.25	2.25	0.563	50.6	212
486	5.47	4.86	2.43	2.43	0.608	54.7	229
500	6.00	5.00	2.50	2.50	0.625	56.3	235

**Table B-2. Energy per Batch and Power Potential for COIL Operation in 1 hour**

MHP Recipe	MHP Batch (kg)	Cl <sub>2</sub> (kg)	I <sub>2</sub> (kg)	Energy Potential (kJ)	Efficiencies		Energy Output (kJ)	Power (kW)	Flowrate		
					Chemical (%)	Extraction (%)			MHP (kg/s)	Cl <sub>2</sub> (kg/s)	Cl <sub>2</sub> (mole/s)
420	10,000	1,489	1,332	1.98 x 10 <sup>6</sup>	25	80	395,010	110	2.78	0.414	5.83
450	10,000	1,595	1,429	2.12 x 10 <sup>6</sup>	25	80	423,225	118	2.78	0.443	6.25
486	10,000	1,723	1,543	2.29 x 10 <sup>6</sup>	25	80	457,083	127	2.78	0.479	6.75
500	10,000	1,773	1,586	2.35 x 10 <sup>6</sup>	25	80	470,250	131	2.78	0.492	6.94

**Notes:**

- a. Energy of singlet oxygen O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>) above the ground state = 22.5 kcal/mol
- b. Molecular weight of Cl<sub>2</sub> = 70.9 g/mol; I<sub>2</sub> = 253.8 g/mol

## Thermal Energy Removal Requirements for BHP Production and SOG Operation

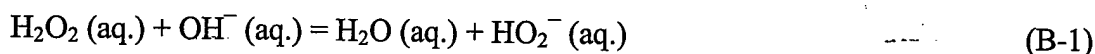
### Heat of Solution for Dissolving Alkali Hydroxides in Water

**Table B-3. Heat of Solution for Dissolving Alkali Hydroxides in Water**

Alkali Hydroxide	MW, g/mol	Heat, kcal/gmol	Heat, cal/g
LiOH	23.95	4.74	197.9
LiOH•H <sub>2</sub> O	41.95	9.6	228.8
NaOH	40.00	10.18	254.5
KOH	56.11	12.91	230.1

### Heat of Reaction for Mixing Alkali Hydroxides with Hydrogen Peroxide

The heat of reaction between a generic metal hydroxide, presumably KOH, and hydrogen peroxide has been reported by Truesdell and Lamberson (1992).



$$\Delta H_{\text{RX1}} = -12 \text{ kcal/gmole } (-50 \text{ kJ/mole}).$$

Based on a recent study, empirical equations have been derived for estimating the heat generated from mixing hydrogen peroxide and mixed-base solutions (i.e., excluding the thermal energy removal requirements for making the base solutions) and base solids (i.e., including the thermal energy removal requirements for making the base solutions). Assuming that (1) the temperature of feed streams = 20°C, (2) process operating temperature = 0°C, and (3) H<sub>2</sub>O<sub>2</sub>/MOH molar ratio = 1.15 to 1. The empirical equations for base solutions and base solids, respectively, are given below.

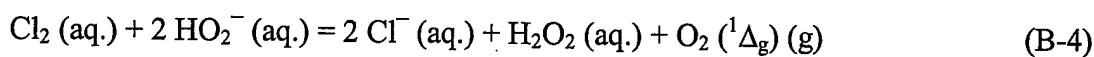
$$Q_{\text{Solution}}/M \text{ (kcal/kg MHP)} = 10 \times [\text{OH}^-] \quad (\text{B-2})$$

$$Q_{\text{Solid}}/M \text{ (kcal/kg MHP)} = 10 \times [\text{OH}^-] + 50 \quad (\text{B-3})$$

where Q is the heat of mixing (kcal), M is the batch weight of MHP (kg), and [OH<sup>-</sup>] is the molar concentration of hydroxide ions in MHP (gmole/kg MHP).

### Heat of Reaction for the Chlorine-BHP Reaction

The reported data on the heat of reaction for the chlorine-BHP reaction, eq B-4, are given below.



$$\Delta H_{\text{RX2}} = -27 \text{ kJ/gmol (Truesdell and Lamberson, 1992)}$$

$$\Delta H_{\text{RX2}} = -26.5 \text{ kJ/gmol (Dickerson et al., 1992)}$$

### Overall Heat Transfer Coefficient

Phipps et al. (1995) reported an overall heat transfer coefficient (U) of 150 BTU/(hr-ft<sup>2</sup>-°F), which was experimentally determined from operating the VertiCOIL system using Syltherm as the cooling medium.

### Calculations on Heat Removal Requirements

**Table B-4. Calculated Heat Removal Requirements for SOG Operation**

Based on 1 kg MHP	Unit	H <sub>2</sub> O <sub>2</sub> -Base	Cl <sub>2</sub> -BHP	Cl <sub>2</sub> -BHP	Cl <sub>2</sub> -BHP	Cl <sub>2</sub> -BHP
	molar basis	KOH	Cl <sub>2</sub>	Cl <sub>2</sub>	Cl <sub>2</sub>	O <sub>2</sub> (Δ)
Heat of Reaction	kcal/mole	12	27	27	27	48
Base Concentration	mole	4.50	4.50	4.50	4.50	4.50
Stoichiometric Cl <sub>2</sub>	mole	-	2.25	2.25	2.25	2.25
Cl <sub>2</sub> Flow Rate*	mole/s	-	<b>0.01</b>	<b>0.1</b>	1	<b>0.01</b>
Run Time	s	3600	225	22.5	2.25	225
Heat Flux**	kcal/s	0.24	0.54	5.4	54	0.96
(at the given Cl <sub>2</sub> flow)	BTU/h	3429	7714	77143	771429	13714
	kW	1.0	2.26	22.6	226	4.02
Mean Temperature	°C	20	20	20	20	20
	°F	68	68	68	68	68
Heat Transfer Area Required Based on the given U***						
SS 316 (U=150)	m <sup>2</sup>	0.0949	0.214	2.14	21.4	0.38
	ft <sup>2</sup>	1.022	2.30	23.0	230	4.09

\* The Cl<sub>2</sub> flow rates given in bold indicate that the values fall within the typical range reported in the literature.

\*\* Assuming 100% singlet oxygen yield, and 100% chlorine utilization.

\*\*\* The unit of the overall heat transfer coefficient U is in BTU/hr-ft<sup>2</sup>-°F.

## Properties of Bases, Hydrogen Peroxide, and Chlorine

This database includes the following properties:

1. Density of Aqueous Solutions of Alkali Hydroxides and Hydrogen Peroxide
2. Heats of Fusion and Evaporation of Selected Compounds at 1 atm
3. Solubility of Alkali Hydroxides and Chlorides in Water
4. Viscosity of Aqueous Solutions of Alkali Hydroxides and Chlorides
5. Freezing Points of Aqueous Solutions of Alkali Hydroxides
6. Thermal Conductivity Aqueous Solutions of Alkali Hydroxides

### Density of Aqueous Solutions (at 15°C)

**Table B-5. Density of Aqueous Solutions (at 15°C)**

Compound	LiOH	NaOH	KOH	H <sub>2</sub> O <sub>2</sub>
1 %		1.01065	1.0083	
2 %		1.02198	1.0175	
4%		1.04441	1.0359	
6%			1.0544	
8%		1.08887	1.073	
10%			1.0918	
12%		1.13327		
15%			1.1396	
20%		1.22183	1.1884	
25%			1.2387	
35% (at 20°C)				1.13
50% (at 20°C)				1.20
70% (at 20°C)				1.29
90% (at 20°C)				1.39

Ref.: Perry's Chemical Engineers' Handbook Table 2-76, 2-90; Hydrogen Peroxide Handbook.

### Heats of Fusion and Evaporation of Selected Compounds at 1 atm

**Table B-6. Heat of Fusion and Evaporation of Selected Compounds (at 1 atm)**

Substance	MW g/mol	m.p. °C	Heat of Fusion cal/mol	S.p. HF cal/g	b.p. °C	Heat of Evaporation cal/mol	S.p. HE cal/g
N <sub>2</sub> , nitrogen	28	-210	172	6.1	-195.8	1336	47.7
NH <sub>3</sub> , ammonia	17	-77.7	1372	80.7	-33.4	5581	328
H <sub>2</sub> O <sub>2</sub> , hydrogen peroxide	34	-2	2520	74.1	158	10270	302
70% HP		-40		75.8	125		
50% HP		-52		77.0	114		
35% HP		-33		77.8	108		
H <sub>2</sub> O, water	18	0	1436	79.8	100	9729	541

Ref.: Perry's Chemical Engineers' Handbook Table 2-190.

Solubility of Alkali Hydroxides and Chlorides in Water

**Table B-7. Solubility of Selected Inorganic Alkali Compounds in Water (g/100 g H<sub>2</sub>O)**

Compound	0°C	10°C	20°C	30°C	40°C	50°C	60°C
LiOH	11.91	12.11	12.35	12.70	13.22		14.63
NaOH	42.0	51.5	109	119	129	145	174
KOH	97	103	112	126	134		154
LiCl	69.2	74.5	83.5	86.2	89.8		98.4
NaCl	35.7	35.8	35.9	36.1	36.4		37.1
KCl	28.0	31.2	34.2	37.2	40.1		45.8
Li <sub>2</sub> CO <sub>3</sub>	1.54	1.43	1.33	1.26	1.17		1.01
NaHCO <sub>3</sub>	6.9	8.2	9.6	11.1	12.7	14.5	16.4
Na <sub>2</sub> CO <sub>3</sub>	7	12.5	21.5	39.7	49		46
KHCO <sub>3</sub>	22.5	27.4	33.7	39.9	47.5		65.6
K <sub>2</sub> CO <sub>3</sub>	105	108	111	114	117		127
LiPO <sub>3</sub>	0.101		0.058		0.048		

Ref.: Lange's Handbook of Chemistry, 14th ed, 1992.

*Italic entries from Crystallization by J.W. Mullin, Butterworth-Heinemann, 1997.*

**Table B-8. Solubility of Selected Inorganic Alkali Compounds in Water (gmol/100g H<sub>2</sub>O)**

Compound	MW	0°C	10°C	20°C	30°C	40°C	60°C
LiOH	23.95	0.497	0.506	0.516	0.530	0.552	0.611
NaOH	40.01	1.050	1.287	2.724	2.974	3.224	4.349
KOH	56.11	1.706	1.836	1.996	2.246	2.388	2.745
LiCl	42.40	1.632	1.757	1.969	2.033	2.118	2.321
NaCl	58.45	0.611	0.612	0.614	0.618	0.623	0.635
KCl	74.56	0.376	0.418	0.459	0.499	0.538	0.614
Li <sub>2</sub> CO <sub>3</sub>	73.89	0.021	0.019	0.018	0.017	0.016	0.014
NaHCO <sub>3</sub>	84.01	0.082	0.098	0.114	0.132	0.151	0.195
Na <sub>2</sub> CO <sub>3</sub>	106	0.066	0.118	0.203	0.375	0.462	0.434
KHCO <sub>3</sub>	100.11	0.225	0.274	0.337	0.399	0.474	0.655
K <sub>2</sub> CO <sub>3</sub>	138.2	0.760	0.781	0.803	0.825	0.847	0.919

Ref: Lange's Handbook of Chemistry, 14th ed, 1992

Viscosity of Alkali Hydroxides and Chlorides in Water

Figure B-6 and Figure B-7 (Occidental Chemical Corporation Chemical Handbooks)

Freezing Points of Aqueous Solutions of Alkali Hydroxides

Figure B-8, Figure B-9 (Occidental Chemical Corp. Chemical Handbooks)  
and Figure B-10 (Pickering, 1893)

Thermal Conductivity of Aqueous Solutions of Alkali Hydroxides and Chlorides

Figure B-11 and Tables B-9 to B-13 (Zaytsev and Aseyev, 1992)

Table B-9. Thermal Conductivity of Aqueous Solution of KOH (Zaytsev and Aseyev, 1992)

		Temperature, °C										W/(m K)
C, %	0	5	10	15	20	25	30	35	40	45		
2	0.552	0.564	0.575	0.586	0.600	0.608	0.615	0.622	0.629	0.642		
4	0.553	0.565	0.577	0.588	0.601	0.609	0.616	0.623	0.630	0.643		
6	0.554	0.566	0.578	0.589	0.602	0.610	0.617	0.624	0.631	0.644		
8	0.555	0.567	0.579	0.590	0.603	0.611	0.618	0.625	0.632	0.645		
10	0.555	0.568	0.579	0.590	0.603	0.611	0.618	0.625	0.632	0.645		
12	0.555	0.568	0.579	0.590	0.603	0.610	0.618	0.625	0.632	0.645		
14	0.555	0.567	0.578	0.589	0.603	0.609	0.617	0.625	0.632	0.645		
16	0.554	0.566	0.577	0.588	0.602	0.608	0.616	0.623	0.630	0.643		
18	0.552	0.544	0.576	0.587	0.601	0.607	0.615	0.622	0.629	0.642		
C, %	50	55	60	65	70	75	80	85	90	95	100	
2	0.647	0.653	0.659	0.664	0.668	0.672	0.673	0.676	0.680	0.683	0.686	
4	0.649	0.654	0.660	0.665	0.669	0.673	0.674	0.678	0.681	0.684	0.686	
6	0.650	0.655	0.661	0.666	0.671	0.674	0.675	0.679	0.682	0.685	0.687	
8	0.650	0.656	0.661	0.667	0.671	0.675	0.676	0.679	0.682	0.685	0.687	
10	0.651	0.657	0.662	0.667	0.672	0.675	0.676	0.680	0.683	0.686	0.688	
12	0.651	0.657	0.662	0.667	0.672	0.675	0.676	0.679	0.682	0.685	0.687	
14	0.650	0.655	0.661	0.667	0.671	0.674	0.675	0.679	0.682	0.684	0.687	
16	0.649	0.655	0.660	0.666	0.670	0.673	0.674	0.678	0.680	0.683	0.686	
18	0.647	0.653	0.659	0.665	0.669	0.672	0.673	0.676	0.680	0.682	0.685	
C, %	0	5	10	15	20	25	30	35	40	45		
20	0.551	0.563	0.574	0.585	0.598	0.605	0.614	0.621	0.628	0.640		
22	0.549	0.551	0.572	0.583	0.596	0.605	0.611	0.618	0.625	0.638		
24	0.546	0.558	0.569	0.580	0.593	0.602	0.609	0.616	0.622	0.635		
26	0.543	0.555	0.566	0.577	0.590	0.597	0.605	0.612	0.619	0.632		
28	0.540	0.552	0.563	0.574	0.587	0.594	0.602	0.609	0.616	0.629		
30	0.536	0.548	0.560	0.570	0.583	0.590	0.598	0.605	0.612	0.625		
32	0.533	0.545	0.556	0.567	0.579	0.587	0.595	0.602	0.609	0.622		
34	0.529	0.541	0.552	0.563	0.575	0.583	0.592	0.598	0.605	0.618		
36	0.525	0.537	0.548	0.559	0.575	0.579	0.587	0.594	0.601	0.614		
38	0.522	0.534	0.545	0.556	0.568	0.576	0.583	0.590	0.597	0.610		
40	0.517	0.529	0.540	0.551	0.534	0.571	0.579	0.586	0.593	0.605		
C, %	50	55	60	65	70	75	80	85	90	95	100	
20	0.646	0.652	0.657	0.662	0.667	0.671	0.672	0.675	0.679	0.682	0.685	
22	0.643	0.650	0.654	0.660	0.665	0.668	0.669	0.673	0.676	0.678	0.681	
24	0.640	0.646	0.652	0.658	0.662	0.666	0.667	0.671	0.674	0.676	0.679	
26	0.638	0.644	0.650	0.654	0.659	0.663	0.664	0.668	0.671	0.674	0.676	
28	0.635	0.640	0.646	0.651	0.656	0.659	0.660	0.664	0.668	0.671	0.673	
30	0.631	0.637	0.643	0.647	0.653	0.656	0.657	0.661	0.664	0.667	0.669	
32	0.628	0.633	0.640	0.644	0.649	0.652	0.653	0.657	0.660	0.664	0.665	
34	0.623	0.629	0.635	0.639	0.645	0.648	0.650	0.653	0.657	0.660	0.662	
36	0.619	0.625	0.631	0.636	0.640	0.644	0.645	0.649	0.653	0.656	0.659	
38	0.615	0.622	0.626	0.632	0.637	0.641	0.642	0.645	0.649	0.652	0.655	
40	0.611	0.617	0.623	0.628	0.632	0.636	0.637	0.641	0.645	0.649	0.652	

Table B-10. Thermal Conductivity of Aqueous Solution of LiOH (Zaytsev and Aseyev, 1992)

C, %	Temperature, °C										W/(m K)
	0	5	10	15	20	25	30	35	40	45	
2	0.572	0.581	0.590	0.599	0.608	0.617	0.627	0.635	0.643	0.650	
4	0.575	0.584	0.593	0.602	0.612	0.622	0.631	0.640	0.648	0.655	
6	0.577	0.587	0.597	0.607	0.617	0.626	0.636	0.644	0.653	0.660	
8	0.581	0.591	0.601	0.611	0.621	0.631	0.641	0.649	0.657	0.665	
10	0.586	0.596	0.606	0.616	0.626	0.635	0.645	0.654	0.662	0.669	

Table B-11. Thermal Conductivity of Aqueous Solution of NaCl (Zaytsev and Aseyev, 1992)

C, %	Temperature, °C										
	0	5	10	15	20	25	30	35	40	45	
5	0.545	0.557	0.568	0.580	0.592	0.601	0.611	0.619	0.627	0.634	
10	0.541	0.552	0.564	0.575	0.588	0.597	0.606	0.614	0.622	0.629	
15	0.537	0.548	0.559	0.571	0.583	0.592	0.601	0.609	0.617	0.624	
20	0.532	0.544	0.555	0.566	0.578	0.587	0.597	0.604	0.612	0.619	
25	0.528	0.539	0.550	0.562	0.574	0.583	0.592	0.600	0.607	0.614	
C, %	50	55	60	65	70	75	80	85	90	95	100
5	0.651	0.646	0.652	0.656	0.660	0.664	0.667	0.669	0.673	0.674	0.675
10	0.636	0.641	0.647	0.650	0.655	0.658	0.662	0.664	0.668	0.669	0.670
15	0.631	0.636	0.642	0.645	0.650	0.653	0.657	0.659	0.662	0.663	0.665
20	0.626	0.631	0.637	0.640	0.645	0.648	0.651	0.654	0.657	0.658	0.659
25	0.621	0.626	0.632	0.635	0.640	0.643	0.646	0.649	0.652	0.653	0.654

Table B-12. Thermal Conductivity of Aqueous Solution of KCl (Zaytsev and Aseyev, 1992)

C, %	Temperature, °C									
	0	5	10	15	20	25	30	35	40	45
2	0.552	0.563	0.575	0.586	0.599	0.609	0.618	0.626	0.634	0.641
4	0.550	0.562	0.574	0.585	0.598	0.607	0.617	0.625	0.633	0.640
6	0.649	0.651	0.672	0.684	0.597	0.606	0.615	0.623	0.632	0.639
8	0.548	0.560	0.571	0.583	0.596	0.605	0.614	0.622	0.630	0.637
10	0.547	0.559	0.570	0.582	0.594	0.603	0.613	0.621	0.629	0.636
12	0.546	0.557	0.569	0.580	0.593	0.602	0.612	0.620	0.628	0.634
14	0.545	0.556	0.568	0.579	0.592	0.601	0.610	0.618	0.626	0.633
16	0.544	0.555	0.566	0.578	0.590	0.600	0.609	0.617	0.625	0.632
18	0.542	0.554	0.565	0.577	0.589	0.598	0.608	0.616	0.624	0.630
20	0.541	0.553	0.564	0.575	0.588	0.597	0.606	0.614	0.622	0.629
22	0.540	0.551	0.563	0.574	0.587	0.596	0.605	0.613	0.621	0.628
24	-	0.550	0.562	0.573	0.585	0.595	0.604	0.612	0.620	0.626
26	-	-	-	-	-	-	0.602	0.610	0.618	0.625

Table B-13. Thermal Conductivity of Aqueous Solution of LiCl (Zaytsev and Aseyev, 1992)

C, %	Temperature, °C										W/(m K)
	0	5	10	15	20	25	30	35	40	45	
2	0.551	0.563	0.574	0.585	0.595	0.604	0.613	0.621	0.629	0.636	
4	0.548	0.560	0.571	0.581	0.591	0.600	0.609	0.617	0.624	0.631	
6	0.545	0.557	0.568	0.578	0.587	0.596	0.605	0.613	0.620	0.627	
8	0.543	0.554	0.564	0.574	0.584	0.593	0.601	0.608	0.615	0.622	
10	0.540	0.551	0.561	0.571	0.580	0.589	0.597	0.604	0.611	0.617	
12	0.537	0.548	0.558	0.568	0.577	0.585	0.593	0.600	0.607	0.613	
14	0.524	0.545	0.555	0.564	0.573	0.581	0.589	0.596	0.602	0.608	
16	0.531	0.542	0.552	0.561	0.569	0.577	0.585	0.592	0.598	0.604	
18	0.529	0.539	0.548	0.557	0.566	0.574	0.581	0.588	0.594	0.599	
C, %	50	55	60	65	70	75	80	85	90	95	100
2	0.642	0.648	0.654	0.658	0.662	0.666	0.669	0.671	0.673	0.674	0.675
4	0.638	0.643	0.648	0.653	0.657	0.660	0.663	0.665	0.666	0.667	0.668
6	0.633	0.638	0.643	0.647	0.651	0.654	0.657	0.659	0.660	0.661	0.661
8	0.628	0.633	0.638	0.642	0.645	0.648	0.651	0.652	0.654	0.654	0.654
10	0.623	0.628	0.632	0.636	0.640	0.642	0.645	0.646	0.647	0.648	0.650
12	0.618	0.623	0.627	0.631	0.634	0.637	0.639	0.640	0.642	0.645	0.648
14	0.613	0.618	0.622	0.626	0.629	0.631	0.633	0.634	0.635	0.637	0.639
16	0.609	0.613	0.617	0.620	0.623	0.625	0.627	0.628	0.629	0.631	0.635
18	0.604	0.608	0.612	0.615	0.618	0.620	0.621	0.622	0.623	0.625	0.629
C, %	0	5	10	15	20	25	30	35	40	45	
20	0.526	0.536	0.545	0.554	0.562	0.570	0.577	0.583	0.589	0.595	
22	0.523	0.533	0.542	0.551	0.559	0.566	0.573	0.579	0.585	0.590	
24	0.520	0.530	0.539	0.547	0.555	0.563	0.569	0.575	0.581	0.586	
26	0.518	0.527	0.536	0.544	0.552	0.559	0.565	0.571	0.577	0.581	
28	0.515	0.524	0.533	0.541	0.548	0.555	0.562	0.567	0.572	0.577	
30	0.512	0.521	0.530	0.538	0.545	0.552	0.558	0.563	0.568	0.573	
32	0.509	0.518	0.527	0.535	0.545	0.548	0.554	0.559	0.564	0.568	
34	0.507	0.516	0.524	0.531	0.538	0.545	0.550	0.556	0.560	0.564	
36	0.504	0.513	0.521	0.528	0.535	0.541	0.547	0.552	0.556	0.560	
38	0.502	0.510	0.518	0.525	0.532	0.538	0.543	0.548	0.552	0.556	
40	0.499	0.507	0.515	0.522	0.528	0.534	0.539	0.544	0.548	0.552	
C, %	50	55	60	65	70	75	80	85	90	95	100
20	0.599	0.603	0.607	0.610	0.612	0.614	0.616	0.616	0.618	0.620	0.622
22	0.595	0.599	0.602	0.605	0.607	0.609	0.610	0.611	0.613	0.616	0.619
24	0.590	0.594	0.597	0.600	0.602	0.603	0.604	0.605	0.607	0.609	0.613
26	0.586	0.589	0.592	0.595	0.597	0.598	0.599	0.602	0.609	0.608	0.612
28	0.581	0.584	0.587	0.590	0.591	0.593	0.594	0.596	0.599	0.603	0.607

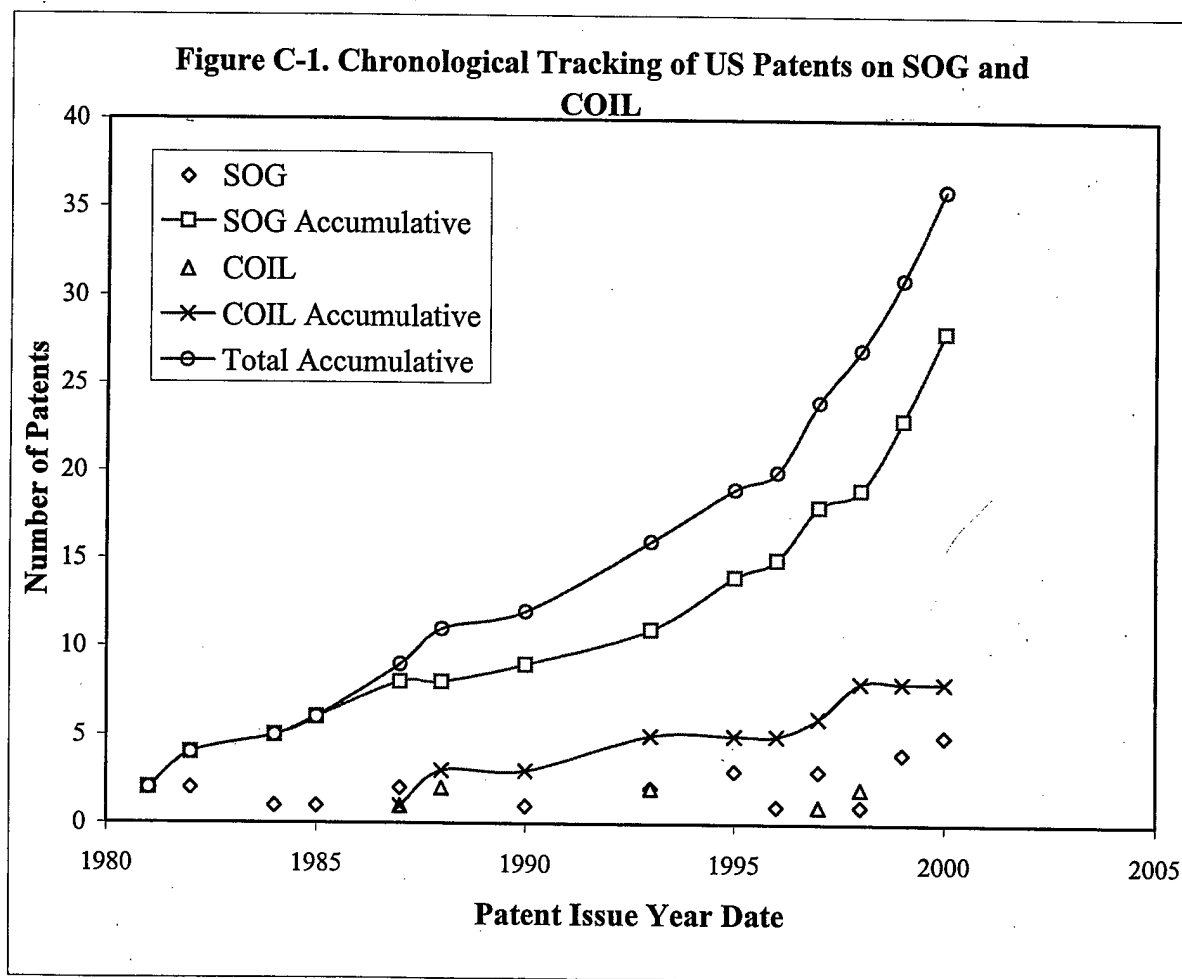
Table B-14. Rate Coefficients for Reactions Associated with COIL Devices (Perram, 1994)

Rxn	Kinetic Process	$k_f$	S
1	$O_2(a^1\Delta) + O_2(a^1\Delta) \rightarrow O_2(b^1\Sigma) + O_2(X^3\Sigma)$	$2.7 \times 10^{-17}$	1
2	$O_2(a^1\Delta) + O_2(a^1\Delta) \rightarrow O_2(a^1\Delta) + O_2(X^3\Sigma)$	0	3
3	$O_2(a^1\Delta) + O_2(a^1\Delta) \rightarrow O_2(X^3\Sigma) + O_2(X^3\Sigma)$	$1.7 \times 10^{-17}$	3
4	$O_2(b^1\Sigma) + O_2(X^3\Sigma) \rightarrow O_2(a^1\Delta) + O_2(X^3\Sigma)$	$3.9 \times 10^{-17}$	3
5	$O_2(b^1\Sigma) + H_2O \rightarrow O_2(a^1\Delta) + H_2O$	$6.7 \times 10^{-12}$	1
6	$O_2(b^1\Sigma) + Cl_2 \rightarrow O_2(a^1\Delta) + Cl_2$	$2.0 \times 10^{-15}$	3
7	$O_2(b^1\Sigma) + H_2O_2 \rightarrow O_2(a^1\Delta) + H_2O_2$	$3.3 \times 10^{-13}$	3
8	$O_2(b^1\Sigma) + He \rightarrow O_2(a^1\Delta) + He$	$1.0 \times 10^{-17}$	3
14	$O_2(a^1\Delta) + O_2(X^3\Sigma) \rightarrow O_2(X^3\Sigma) + O_2(X^3\Sigma)$	$1.6 \times 10^{-18}$	2
15	$O_2(a^1\Delta) + H_2O \rightarrow O_2(X^3\Sigma) + H_2O$	$4.0 \times 10^{-18}$	2
16	$O_2(a^1\Delta) + Cl_2 \rightarrow O_2(X^3\Sigma) + Cl_2$	$6.0 \times 10^{-18}$	2
17	$O_2(a^1\Delta) + H_2O_2 \rightarrow O_2(X^3\Sigma) + H_2O_2$	0	3
18	$O_2(a^1\Delta) + He \rightarrow O_2(X^3\Sigma) + He$	$8.0 \times 10^{-21}$	2
21	$I_2(X^1\Sigma) + O_2(b^1\Sigma) \rightarrow I + I + O_2(X^3\Sigma)$	$4.0 \times 10^{-12}$	1
22	$I_2(X^1\Sigma) + O_2(b^1\Sigma) \rightarrow I_2(X^1\Sigma) + O_2(a^1\Delta)$	0	2
23	$I_2(X^1\Sigma) + O_2(b^1\Sigma) \rightarrow I_2(X^1\Sigma) + O_2(X^3\Sigma)$	0	3
24	$I_2(X^1\Sigma) + O_2(b^1\Sigma) \rightarrow I_2(A,A') + O_2(X^3\Sigma)$	$1.6 \times 10^{-11}$	3
25	$I_2(A,A') + O_2(a^1\Delta) \rightarrow I + I + O_2(X^3\Sigma)$	$1.0 \times 10^{-11}$	3
26	$I_2(A,A') + O_2(a^1\Delta) \rightarrow I_2(B^3\Pi) + O_2(X^3\Sigma)$	$8.0 \times 10^{-11}$	3
30	$I_2(B^3\Pi) \rightarrow I + I$	$6 \times 10^{-5} \text{ s}^{-1}$	3
31	$I_2(B^3\Pi) \rightarrow I_2(X^1\Sigma) + h\nu$	$6 \times 10^{-5} \text{ s}^{-1}$	3
32	$I_2(X^1\Sigma) + O_2(a^1\Delta) \rightarrow I_2^* + O_2(X^3\Sigma)$	$7.0 \times 10^{-15}$	1
33	$I_2(X^1\Sigma) + I^* \rightarrow I_2^* + I$	$3.8 \times 10^{-11}$	1
34	$I_2^* + O_2(a^1\Delta) \rightarrow I + I + O_2(X^3\Sigma)$	$3.0 \times 10^{-10}$	1
35	$I_2^* + O_2(X^3\Sigma) \rightarrow I_2(X^1\Sigma) + O_2(X^3\Sigma)$	$5.0 \times 10^{-11}$	2
36	$I_2^* + H_2O \rightarrow I_2(X^1\Sigma) + H_2O$	$3.0 \times 10^{-10}$	1
37	$I_2^* + He \rightarrow I_2(X^1\Sigma) + He$	$4.0 \times 10^{-12}$	2
40	$I + O_2(a^1\Delta) \rightarrow I^* + O_2(X^3\Sigma)$	$7.8 \times 10^{-11}$	1
41	$I^* + O_2(X^3\Sigma) \rightarrow I + O_2(a^1\Delta)$	$2.7 \times 10^{-11}$	1
42	$I + O_2(a^1\Delta) \rightarrow I + O_2(X^3\Sigma)$	$1.0 \times 10^{-15}$	2
43	$I^* + O_2(X^3\Sigma) \rightarrow I + O_2(X^3\Sigma)$	0	3
44	$I^* + O_2(a^1\Delta) \rightarrow I + O_2(b^1\Sigma)$	$1.1 \times 10^{-13}$	1
45	$I^* + O_2(a^1\Delta) \rightarrow I + O_2(a^1\Delta)$	$1.1 \times 10^{-13}$	2
46	$I^* + O_2(a^1\Delta) \rightarrow I + O_2(X^3\Sigma)$	0	3
47	$I^* + I \rightarrow I + I$	$1.6 \times 10^{-14}$	2
48	$I^* + H_2O \rightarrow I + H_2O$	$2.0 \times 10^{-12}$	1
49	$I^* + H_2O_2 \rightarrow I + H_2O_2$	$2.5 \times 10^{-11}$	3
50	$I^* + He \rightarrow I + He$	$5.0 \times 10^{-18}$	3
51	$I^* + O_2(X^3\Sigma) \rightarrow I + O_2(X^3\Sigma)$	$3.5 \times 10^{-16}$	2
53	$I^* \rightarrow I + h\nu$	$7.8 \text{ s}^{-1}$	3
54	$I^* + Cl_2 \rightarrow ICl + Cl$	$5.5 \times 10^{-15}$	3
56	$I^* + ICl \rightarrow I_2 + Cl$	$1.5 \times 10^{-11}$	3
57	$I_2 + Cl \rightarrow ICl + I$	$2.0 \times 10^{-10}$	3
58	$ICl + Cl \rightarrow Cl_2 + I$	$8.0 \times 10^{-12}$	3
59	$I + I + I_2(X^1\Sigma) \rightarrow I_2(X^1\Sigma) + I_2(X^1\Sigma)$	$3.6 \times 10^{-30}$	3
60	$I^* + I + I_2(X^1\Sigma) \rightarrow I_2(B^3\Pi) + I_2(X^1\Sigma)$	$3.6 \times 10^{-30}$	3
61	$I + I + He \rightarrow I_2(X^1\Sigma) + He$	$3.6 \times 10^{-33}$	3
62	$I + I + O_2(X^3\Sigma) \rightarrow I_2(X^1\Sigma) + O_2(X^3\Sigma)$	$3.7 \times 10^{-32}$	3

Standard COIL Kinetics Package  
(Rate Coefficients in  $\text{cm}^3/\text{molecule-s}$ )

### Appendix C: U.S. Patents on Singlet Oxygen Generators

A preliminary search was performed in the U.S. patent database ([www.delphion.com](http://www.delphion.com)) using the key words of singlet oxygen, singlet oxygen generation/generator, and chemical oxygen-iodine laser. A total of 38 patents that deal with processes involving the chlorine-BHP reaction were found. Among these selected entries, 20 patents are related to SOG, five patents deal with BHP production and regeneration, four patents address auxiliary components of SOG, eight patents cover COIL (mainly iodine injector/mixer), and one patent describes a measurement method for singlet oxygen. Figure C-1 shows the chronological tracking of these US patents. Furthermore, the basic information of these US patents, except for those covering COIL, is summarized below according to the chronological order of the patent issue date. The summary for each selected patent includes the inventor name(s), title, patent number, abstracts, first claims, assignee, and filing date.



**U.S. Patents Dealing with SOG based on the Chlorine-BHP Reaction**

- Beshore and Stelman,2000,Salt Free Lithium Hydroxide Base for Chemical Oxygen Iodine Lasers,6,010,640
- Clendening, English,1999,Gas Generating System for Chemical Lasers,5,859,863
- Clendening, English,1997,Gas Generating System for Chemical Lasers,5,624,654
- Clendening, English,1999,Gas Generating System for Chemical Lasers,5,925,286
- Clendening, Hartlove,2000,Water Vapor Trap and Liquid Separator for Singlet-Delta Oxygen Generator,6,165,424
- Davis,1987,Supersonic Singlet Delta Oxygen Aerosol Generator,4,668,498
- Dickerson,1996,Singlet Delta Oxygen Generator,5,516,502
- Dickerson,2000,Chemical Oxygen Iodine Laser Gain Generator System,6,072,820
- Dinges,1995,Formation of Basic Hydrogen Peroxide,5,378,449
- Harpole,1993,Rotating Disk Singlet Oxygen Generator,5,229,100
- Hartlove,2000,Singlet-Delta Oxygen Generator,6,099,805
- Hed,1990,"Delta Singlet Oxygen" Continuous Reactor,4,975,265
- Hed,1993,Delta Singlet Oxygen Continuous Reactor,5,246,673
- Lohn and Schlichting,1999,Integrated Valve and Flow Control Apparatus and Method for Chemical Laser System.,5,883,916
- Lonergan and Horrocks,1997,Regeneration of BHP in a Plant Process,5,658,488
- MacKnight and Stancliffe,1982,Dry Excited Singlet Delta Oxygen Generator,4,342,116
- McDermott,1995,Singlet Delta Oxygen Generator and Process,5,417,928
- McDermott, Benard,1981,Continuous Wave Chemically Pumped Atomic Iodine Laser, 4,267,526
- McDermott, Benard,1981,Gas Generating System for Chemical Lasers,4,246,252
- McDermott, Ellis,1985,Tubular Singlet Delta Oxygen Generator,4,558,451
- Richardson and Lilenfeld,1982,Process for Generating Singlet-Oxygen,4,318,895
- Rockenfeller,1984,Singlet Delta Oxygen Generator,4,461,756
- Schall,1998,Oxygen-iodine laser,5,802,095
- Stelman,2001,Elimination of Anomalous Freezing of Basic Hydrogen Peroxide in the Chemical Oxygen Iodine Laser,6,224,786
- Thayer,1995,Uniform Droplet Generator,5,392,988
- Thayer,1997,Transverse Flow Uniform Droplet O<sub>2</sub> (<sup>1</sup>.DELTA.) Generator and Method for its Use.,5,658,535
- Uchiyama, Takehisa,1987,System for Generation of Singlet-Delta Oxygen,4,643,889
- Vetrovec,1999,Method of Operating Electrolytic Cell to Produce Highly Concentrated Alkaline Hydrogen Peroxide.,6,004,449
- Vetrovec,2000,Chemical Oxygen-Iodine Laser (COIL)/Cryosorption Vacuum Pump System,6,154,478
- Wagner,1982,Singlet Delta Oxygen Generator and Process,4,310,502.

**Reference Type:** US Patent

**Record Number:** 29

**Inventor:** Beshore, David G.; Stelman, David

**Year:** 2000

**Title:** Salt Free Lithium Hydroxide Base for Chemical Oxygen Iodine Lasers

**Country:** United States

**Patent Number:** 6,010,640

**Issue Date:** Jan. 4, 2000

**Keywords:** Basic Hydrogen Peroxide (BHP)

**Abstract:** Basic hydrogen peroxide used in chemical oxygen lasers can be produced using a lithium based lithium hydroxide with a lithium hydroxide makeup of the reacted basic hydrogen peroxide. Lithium hydroxide, water and hydrogen peroxide are mixed and 1) passed over a lithium hydroxide solid bed or 2) premixed with small particulate solid lithium hydroxide or lithium hydroxide monohydrate. The basic hydrogen peroxide produced is chilled and stored cold until mixed with chlorine to produce singlet delta oxygen for use in the chemical oxygen iodine laser. The spent basic hydrogen peroxide is rejuvenated by passing it over a solid lithium hydroxide or in-situ solid particulate lithium hydroxides. After dissolution, the rejuvenated basic hydrogen peroxide is then reacted with chlorine to produce more singlet delta oxygen.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. A lithium hydroxide base slurry for producing basic hydrogen peroxide comprising solid and dissolved lithium hydroxide and hydrogen peroxide water solution.

**Assignee:** Boeing North American, Inc., Seal Beach, CA

**Filing Date:** Jul. 15, 1996

**Reference Type:** US Patent

**Record Number:** 32

**Inventor:** Clendening, Charles W., Jr.; English, William D.; Mach, Martin H.

**Year:** 1999

**Title:** Gas Generating System for Chemical Lasers

**Country:** United States

**Patent Number:** 5,859,863

**Issue Date:** Jan. 12, 1999

**Keywords:** Basic Hydrogen Peroxide (BHP), Singlet Oxygen Generator (SOG)

**Abstract:** A system for preparing excited molecular oxygen in the excited singlet-delta electronic state for use in a chemical laser that minimizes salt formation utilizing the common ion effect. In one version, basic hydrogen peroxide is formed by combining  $H_2O_2$  and at least two bases. In another version of the invention, the basic hydrogen peroxide is reacted with a gas containing at least two halogen species.

**First Claim:** What is claimed is:

1. A method for preparing excited molecular oxygen in the excited singlet-delta electronic state for use as an energizing reactant for a chemical laser, the method of comprising the steps of:
  - a) combining  $H_2O_2$  and at least two bases, B1 and B2, to form a reaction mixture containing basic hydrogen peroxide, B1 being selected from the group consisting of alkali metal bases, alkaline earth metal bases, and nitrogen containing bases, and B2 being selected from the group consisting of alkali metal bases and alkaline earth metal bases, the total amount of base being no more than one mole per mole of  $H_2O_2$ ;
  - b) combining the basic hydrogen peroxide with a halogen gas to produce the excited molecular oxygen; and
  - c) continuing the introduction of the halogen gas until the reaction mixture contains less than one molar basic hydrogen peroxide, and wherein the molar ratio of B1 to B2, is selected so that substantially no insoluble salt is formed.

**Assignee:** TRW Inc., Redondo Beach, CA

**Filing Date:** Dec. 9, 1996

**Reference Type:** US Patent

**Record Number:** 20

**Inventor:** Clendening, Charles W., Jr.; English, William D.; Mach, Martin H.; Dreiling, Trecil D.

**Year:** 1997

**Title:** Gas Generating System for Chemical Lasers

**Country:** United States

**Patent Number:** 5,624,654

**Issue Date:** Apr. 29, 1997

**Keywords:** Basic Hydrogen Peroxide (BHP), Singlet Oxygen Generator (SOG)

**Abstract:** A system for preparing excited molecular oxygen in the excited singlet-delta electronic state for use in a chemical laser that minimizes salt formation utilizing the common ion effect. In one version, basic hydrogen peroxide is formed by combining  $H_2O_2$  and at least two bases. In another version of the invention, the basic hydrogen peroxide is reacted with a gas containing at least two halogen species.

**First Claim:** First claim: What is claimed is:

1. A method for preparing excited molecular oxygen in the excited singlet-delta electronic state for use as an energizing reactant for a chemical laser, the method comprising the steps of:

- a) combining  $H_2O_2$  and at least one base to form a reaction mixture containing basic hydrogen peroxide, the base being selected from the group consisting of alkali metal bases, alkaline earth metal bases, and nitrogen containing bases, the total amount of base being no more than one mole per mole of  $H_2O_2$ ; and
- b) introducing the basic hydrogen peroxide into a gas containing at least two halogen species,  $X_1$  and  $X_2$ , selected from the group consisting of chlorine, bromine, and bromine chloride to produce the excited molecular oxygen, the molar ratio of  $X_1$  to  $X_2$  being from about 3:1 to about 1:1.

**Assignee:** TRW Inc., Redondo Beach, CA

**Filing Date:** May 13, 1996

**Reference Type:** US Patent

**Record Number:** 43

**Inventor:** Clendening, Charles W., Jr.; English, William D.; Mach, Martin H.; Dreiling, Trecil D.

**Year:** 1999

**Title:** Gas Generating System for Chemical Lasers

**Country:** United States

**Patent Number:** 5,925,286

**Issue Date:** July 20, 1999

**Keywords:** Basic Hydrogen Peroxide (BHP), Singlet Oxygen Generator (SOG)

**Abstract:** A system for preparing excited molecular oxygen in the excited singlet-delta electronic state for use in a chemical laser that minimizes salt formation utilizing the common ion effect. In one version, basic hydrogen peroxide is formed by combining  $H_2O_2$  and at least two bases. In another version of the invention, the basic hydrogen peroxide is reacted with a gas containing at least two halogen species.

**First Claim:** What is claimed is:

1. A composition of matter for generating molecular oxygen in the excited singlet-delta electronic state comprising a mixture of (i) basic hydrogen peroxide resulting from combining  $H_2O_2$  and at least two different bases B1 and B2, and (ii) at least one halogen species, the bases being selected from the group consisting of alkali metal bases, alkaline earth metal bases, and nitrogen containing bases, wherein at least one of the bases is an alkali metal base, the total amount of bases being no more than one mole per mole of  $H_2O_2$ .

**Assignee:** TRW, Inc., Redondo Beach, Calif.

**Filing Date:** Dec. 1, 1997

**Inventor:** Clendening, Charles W., Jr.; Hartlove, Jeffrey S.; Day, Robert J.  
**Title:** Water Vapor Trap and Liquid Separator for Singlet-Delta Oxygen Generator  
**Country:** United States  
**Patent Number:** 6,165,424  
**Issue Date:** Dec. 26, 2000

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A singlet-delta oxygen generator 10 comprises a chamber 14 in which a gas stream 22 of singlet-delta oxygen, O<sub>2</sub> (1 .DELTA.), is generated; a water vapor trap 40 to remove water vapor from the gas stream, and a liquid separator 60 downstream of the water vapor trap to separate liquid from the gas stream subsequent to removal of the water vapor. The water vapor trap comprises a liquid droplet dispersing device 42 which forms a droplet field 44 of cold liquid droplets in the chamber. The cold liquid droplets interact with and condense water vapor in the gas stream. The cold liquid is preferably hydrogen peroxide. The liquid separator comprises a baffle 62 arrangement which forms a tortuous flow path for the gas stream. Liquid in the gas stream is unable to traverse the baffles and is separated from the liquid, to produce an essentially dry gas stream for introduction into a gain generator 34 downstream of the singlet-delta oxygen generator.

**First Claim:** What is claimed is:

1. A single-delta oxygen generator, comprising:

(a) a chamber generating a gas stream of singlet-delta oxygen, the chamber including a first droplet field and a second droplet field;

(b) a first circulation loop for circulating a first liquid forming the first droplet field, the first droplet field generating the gas stream of singlet-delta oxygen, the first circulation loop including a liquid inlet, a first collector and a first recirculation path; and

(c) a second circulation loop for circulating a second liquid forming the second droplet field, the second droplet field interacting with the gas stream such that water vapor contained in the gas stream is condensed, the second circulation loop including a source of the second liquid, a water vapor trap, a second collector and a second recirculation path, wherein the second collector collects the second liquid after the gas stream has passed through the second droplet field, and wherein the water vapor trap reduces the water vapor content of the collected second liquid.

**Assignee:** TRW Inc., Redondo Beach, CA  
**Filing Date:** Jul. 9, 1997

**Inventor:** Davis, James A.  
**Title:** Supersonic Singlet Delta Oxygen Aerosol Generator  
**Country:** United States  
**Patent Number:** 4,668,498  
**Issue Date:** May 26, 1987

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A singlet delta aerosol generator 10 includes a reaction chamber 24 downstream from a supersonic nozzle section 18. A mixture of gaseous chlorine and an inert diluent gas is reacted with liquid basic hydrogen peroxide (BHP) in reaction chamber 24 to form a flow of liquid droplets and gaseous singlet delta oxygen. Separating means, including a deflecting body 30, located within a downstream end of the reaction chamber 24, separates the flow of liquid droplets and gaseous singlet delta oxygen into a primary flow and a secondary flow. The primary flow contains a major amount of the gaseous singlet delta oxygen and a minor amount of the liquid droplets; the secondary flow contains the remainder of the gaseous singlet delta oxygen and of liquid droplets.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. A method for generating singlet delta oxygen comprising the steps of:  
 reacting gaseous chlorine with liquid basic hydrogen peroxide (BHP) under supersonic flow conditions to form a flow of liquid droplets and gaseous singlet delta oxygen; and separating said flow of liquid droplets and gaseous singlet delta oxygen into a primary flow and a secondary flow, said primary flow containing a major amount of said gaseous singlet delta oxygen and a minor amount of said droplets, said secondary flow containing the remainder of said gaseous singlet delta oxygen and of said liquid droplets.

**Assignee:** None  
**Filing Date:** Sep. 27, 1985

**Inventor:** Dickerson, Robert A.

**Title:** Singlet Delta Oxygen Generator

**Country:** United States

**Patent Number:** 5,516,502

**Issue Date:** May 14, 1996

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A method and apparatus for generating excited singlet delta oxygen by effecting a chemical reaction between chlorine and basic hydrogen peroxide.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. A method of producing singlet delta oxygen comprising the steps of:

(a) injecting reactants comprising liquid basic hydrogen peroxide and gaseous chlorine at supersonic speed into a reactor having a constant circular cross section;

(b) reacting the injected gaseous chlorine with the injected liquid basic hydrogen peroxide under supersonic flow conditions within the reactor in a cyclonic manner to form a flow of liquid droplets and gaseous singlet delta oxygen, the gaseous chlorine being injected tangentially to an outer radius of said reaction chamber via jets opening into said chamber near an inner radial wall thereof; and

(c) separating said flow of liquid droplets and gaseous singlet delta oxygen into distinct separate flow streams.

**Assignee:** Rockwell International Corp., Seal Beach, CA.

**Filing Date:** Dec. 10, 1992

**Inventor:** Dickerson, Robert A.

**Title:** Chemical Oxygen Iodine Laser Gain Generator System

**Country:** United States

**Patent Number:** 6,072,820

**Issue Date:** Jun. 6, 2000

**Keywords:** Singlet Oxygen Generator (SOG), Iodine Injector

**Abstract:** The COIL gain generator system includes a reactor for producing singlet delta oxygen and a mechanism for mixing high momentum diluent with the singlet delta oxygen and with iodine for producing a high momentum, low static temperature mixture of the singlet delta oxygen, diluent and iodine. The singlet delta oxygen and the iodine react to produce excited iodine atoms which can lase efficiently due to the low static temperature and can, after lasing, recover to high pressure in a diffuser due to the high momentum of the mixture. This provides the capability of using a chemical pump which allows a completely sealed system with no outside exhaust.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. A chemical oxygen iodine laser gain generator system, comprising:

a) a reactor for producing singlet delta oxygen; and

b) means for mixing high momentum diluent with said singlet delta oxygen and with iodine for producing a high momentum, low static temperature mixture of the singlet delta oxygen, diluent and iodine, wherein the singlet delta oxygen and the iodine react to produce excited iodine atoms which can lase efficiently due to the low static temperature and can, after lasing, recover to high pressure in a diffuser due to the high momentum of the mixture.

**Assignee:** The Boeing Company, Seal Beach, CA

**Filing Date:** Apr. 16, 1998

**Inventor:** Dinges, Warren L.  
**Title:** Formation of Basic Hydrogen Peroxide  
**Country:** United States  
**Patent Number:** 5,378,449  
**Issue Date:** Jan. 3, 1995

**Keywords:** Basic Hydrogen Peroxide (BHP)

**Abstract:** Potassium superoxide can be used to generate and regenerate Basic Hydrogen Peroxide, the primary fuel for Chemical Oxygen-Iodine Lasers. The solid reacts with depleted BHP/H<sub>2</sub>O<sub>2</sub> solution consuming one equivalent of hydrogen peroxide and producing two equivalents of hydroperoxide, reversing the chlorine/BHP reaction that evolves singlet delta oxygen, the energetic species in the COIL system. This same regeneration reaction can be used to generate new BHP solutions by reaction of potassium superoxide with dilute hydrogen peroxide or a protic mineral acid such as hydrochloric acid. These reactions of potassium superoxide provide new and useful methods of generating and regenerating BHP, that significantly decrease COIL system weights and environmental impact.

**First Claim:** What is claimed is:

1. A method for generating basic hydrogen peroxide (BHP) by reacting potassium superoxide with an acid selected from the group consisting of hydrogen peroxide and a protic acid.

**Assignee:** The United States of America as represented by the Secretary of the Air Force  
**Filing Date:** Aug. 31, 1993

**Inventor:** Harpole, George M.  
**Title:** Rotating Disk Singlet Oxygen Generator  
**Country:** United States  
**Patent Number:** 5,229,100  
**Issue Date:** Jul. 20, 1993

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A rotating disk reactor for producing singlet delta oxygen is disclosed. The reactor includes a plurality of closely spaced coaxial disks partially immersed in a pool of liquid basic hydrogen peroxide (BHP) inside a reactor vessel. A thin film of BHP is picked up and carried on the rotating disks. Chlorine gas, diluted with helium, is flowed into the reactor vessel to pass between the disks and react with the BHP to produce singlet delta oxygen. The singlet delta oxygen flows out of the reactor through a liquid separator to remove liquids and then through an impurity cold trap to remove by condensation gaseous H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O.

**First Claim:** I claim

1. A method for generating singlet delta oxygen, comprising the steps of:
  - (a) providing an enclosure;
  - (b) providing a plurality of closely spaced coaxial disks inside the enclosure;
  - (c) partially filling the enclosure with aqueous basic H<sub>2</sub>O<sub>2</sub> to a sufficient level so that the disks are partially immersed in the aqueous basic H<sub>2</sub>O<sub>2</sub> ;
  - (d) rotating the disks so that a film of the aqueous basic H<sub>2</sub>O<sub>2</sub> is formed and carried on non-immersed portions of the disks; and,
  - (e) flowing chlorine gas between the non-immersed portions of the rotating disks to react with the aqueous basic H<sub>2</sub>O<sub>2</sub> to produce singlet delta oxygen.

**Assignee:** The United States of America as represented by the Secretary of the Air Force.  
**Filing Date:** June 13, 1988

**Inventor:** Hartlove, Jeffrey S.

**Title:** Singlet-Delta Oxygen Generator

**Country:** United States

**Patent Number:** 6,099,805

**Issue Date:** Aug. 8, 2000

**Keywords:** Singlet oxygen generator (SOG)

**Abstract:** A singlet-delta oxygen generator suitable for use in a COIL-type chemical laser system is provided wherein the generator has a gaseous reactant distributor which includes (a) side, top and bottom walls to form a distribution chamber; (b) a thin distribution plate disposed vertically within one of the side walls adjacent to the falling droplet zone, the distribution plate having a plurality of holes to allow the passage of gaseous first reactant therethrough; (c) a plurality of gaseous first reactant inlet openings for allowing the influx of gaseous first reactant into the distribution chamber; and (d) a liquid drain disposed in the bottom wall. In a preferred embodiment of the invention, the gaseous reactant inlet openings are conduits which direct the influx of gaseous first reactant away from the distribution plate. The invention allows that (i) gaseous first reactant can be flowed into the distribution chamber via the gaseous reactant inlet openings in a manner such that the distribution of gaseous reactant within the distribution chamber is substantially uniform, (ii) the gaseous first reactant can be allowed to flow laterally through the holes in the distribution plate and into droplets of the liquid second reactant falling downwardly within the falling droplet zone, and (iii) any liquid entering the distribution chamber can be promptly drained away via the liquid drain.

**First Claim:** What is claimed is:

1. In a singlet delta oxygen generator for reacting a gaseous first reactant with falling droplets of a liquid second reactant in a falling droplet zone, the improvement comprising the use in the generator of a gaseous reactant distributor comprising:

- (a) side, top and bottom walls to form a distribution chamber;
- (b) a distribution plate disposed vertically within one of the side walls adjacent to the falling droplet zone, the distribution plate having a plurality of holes to allow the passage of gaseous first reactant there through;
- (c) a plurality of gaseous first reactant inlet openings for allowing the influx of the gaseous first reactant into the distribution chamber such that the distribution of the gaseous first reactant is substantially uniform; and
- (d) a liquid drain disposed in the bottom wall; wherein (i) the gaseous first reactant can be allowed to flow laterally through the holes in the distribution plate and into droplets of the liquid second reactant falling downwardly within the falling droplet zone, and (ii) wherein liquid entering the distribution chamber can be promptly drained away via the liquid drain.

**Assignee:** TRW Inc., Redondo Beach, CA

**Filing Date:** July 9, 1997

**Inventor:** Hed, Aharon Z.

**Title:** "Delta Singlet Oxygen" Continuous Reactor

**Country:** United States

**Patent Number:** 4,975,265

**Issue Date:** Dec. 4, 1990

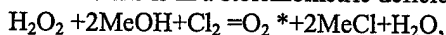
**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A reactor capable of continuously producing activated species of oxygen molecules, specifically those known as "Delta Singlet Oxygen". Uses of "Delta Singlet Oxygen" include the maintenance of high oxidation potential during the deposition of layers of high temperature superconductors. Delta singlet oxygen is particularly effective in obtaining ultra-smooth surfaces when used as the etching gas in plasma milling of a diamond-like carbon film. The film can be used as an ideal insulating barrier for construction of high-temperature superconducting Josephson junctions.

**First Claim:** I Claim:

1. A process for the continuous production of delta singlet oxygen, comprising the steps of:
- (a) continuously forming an aerosol of a mixture of hydrogen peroxide and an alkali-metal hydroxide; (b) continuously directing said aerosol and chlorine gas in opposite directions against each other into mutually impinging relationship in a gas-filled reaction zone in a reactor to react said mixture with said chlorine gas and produce said delta singlet oxygen;

- (c) providing a free gas-filled space directly above said zone in said reactor into which said delta singlet oxygen directly passes upwardly from said reaction zone, and removing said delta singlet oxygen from said reactor and said space without causing said delta singlet oxygen to pass through a body of liquid;
- (d) permitting droplets of reaction products other than delta singlet oxygen to freely fall downwardly in said vessel; and
- (e) controlling the proportions of said hydrogen peroxide alkali-metal hydroxide and chlorine gas at said zone so that said chlorine is in a stoichiometric deficiency for the reaction



where Me is alkali metal and  $\text{O}_2^*$  is delta singlet oxygen.

**Assignee:** International Superconductor Corp., Riverdale, NY.

**Filing Date:** Dec. 21, 1988

**Inventor:** Hed, Aharon Z.

**Title:** Delta Singlet Oxygen Continuous Reactor

**Country:** United States

**Patent Number:** 5,246,673

**Issue Date:** Sep. 21, 1993

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A reactor capable of continuously producing activated species of oxygen molecules, specifically those known in the prior art as "Delta Singlet Oxygen". Uses of "Delta Singlet Oxygen" include the maintenance of high oxidation potential during the deposition of layers of high temperature superconductors. Such species are particularly effective in obtaining ultra smooth surfaces when used as the etching gas in plasma milling of a diamond-like carbon film. The use of a film of this type has been found to be the ideal insulating barrier for construction of high temperature superconducting Josephson junctions. The reactor uses toroidal pipes to generate mutual impingement between a reaction machine and chlorine gas.

**First Claim:** I claim:

1. An apparatus for the continuous production of delta singlet oxygen, comprising:
  - a reactor;
  - a source of chlorine gas;
  - means for continuously feeding a mixture of hydrogen peroxide and an alkali-metal hydroxide to said reactor;
  - chlorine gas feed means connected to said source for feeding chlorine gas to said reactor;
  - means in said reactor for forming an aerosol from said mixture and for directing said aerosol and chlorine gas into mutually impinging relationship in a reaction zone to react said mixture with said chlorine gas and produce said delta singlet oxygen,
  - said means in said reactor for forming an aerosol from said mixture and for directing said aerosol and chlorine gas into mutually impinging relationship in said reaction zone including respective toroidal pipes respectively connected to said means for continuously feeding and to said chlorine gas feed means, said toroidal pipes having respective arrays of nozzles training respective jets of said mixture and said chlorine gas directly against one another; and
  - means for recovering said delta singlet oxygen in a delta singlet oxygen stream from said reaction zone of said reactor.

**Assignee:** Troy Investments Inc., Nashua, NH

**Filing Date:** Jan. 15, 1992

**Inventor:** Lohn, Peter D.; Schlichting, Robert A.

**Title:** Integrated Valve and Flow Control Apparatus and Method for Chemical Laser System.

**Country:** United States

**Patent Number:** 5,883,916

**Issue Date:** March 16, 1999

**Keywords:** Singlet Oxygen Generator (SOG); Flow control device

**Abstract:** There is provided a cylindrical valve 20 for placement in the flow path of a singlet-delta oxygen generator 12 that feeds  $O_2^*$  to a chemical laser gain medium 14. The feed path 22 includes a sharp  $90^\circ$  bend 24 that causes fluid velocity variations in  $O_2^*$  entering the gain medium 14. Integral with the valve 20 is a tubular structure 12 having a partial circumferential radially extending surface 44 fitted with "O" ring for sealing and opening the feed path between the " $O_2^*$ " generator 12 and gain generator 14. A series of vanes 32, 34, 36 disposed in velocity control zones 50, 52, 54 and 56 are integral with the valve 20 for leveling out the velocity variations and controlling the wake formation 58, 59 and 60 in the  $O_2^*$  entering the gain generator 14.

**First Claim:** What is claimed is:

1. In an apparatus for controlling the feed of singlet delta oxygen from a singlet delta oxygen generator to a laser gain generator over a non-rectilinear flow path from a first direction to a second direction, said apparatus comprising:

- a singlet delta oxygen generator;
- a laser gain generator;
- a feed line communicating with said singlet delta oxygen generator with the laser gain generator;
- valve means interposed in said feed line for controlling the feed of said singlet delta oxygen to the laser gain generator in the velocity of the fluid as it proceeds from said first direction to said second direction, said fluid flow control means comprising a series of vanes disposed in the path of the singlet-delta oxygen for maintaining a uniform rate of flow throughout the cross section of the feed line and arranged to minimize the wake formation from the vanes as the singlet-delta oxygen enters said laser gain generator as the fluid changes direction.

**Assignee:** TRW Inc., Redondo Beach, CA

**Filing Date:** Jun. 9, 1997

**Inventor:** Lonergan, Thomas J.; Horrocks, John C.

**Title:** Regeneration of BHP in a Plant Process

**Country:** United States

**Patent Number:** 5,658,488

**Issue Date:** Aug. 19, 1997

**Keywords:** Basic Hydrogen Peroxide (BHP); Singlet Oxygen Generator (SOG)

**Abstract:** Provided is method and apparatus for regenerating basic hydrogen peroxide (BHP) solution. Such solution is run through filters which are alternated for continuous filtration thereof, while the non-used filter is being cleaned. The filtered BHP solution is then reacted with  $H_2 O_2$  and  $KO_2$  or  $KOH$  in a cooled reactor and again filtered and fed to a cooled storage tank as replenished BHP solution. The replenished BHP solution can then be fed to a singlet oxygen generator (SOG) for reaction with  $Cl_2$  to emit singlet delta oxygen (to fuel a COIL laser system) and depleted BHP solution, which is then recycled for filtration and regeneration as before. Thus the process of the invention provides for continuous regeneration of BHP solution for extended use in a COIL. That is, extended COIL run times are required by a COIL for welding and/or cutting operations. At the same time the process of the invention minimizes the amount of BHP required to run the COIL since the BHP is regenerated and recycled. Further, smaller BHP run/mix/storage tanks can be used.

**First Claim:** What is claimed is:

1. A method for the continuous regeneration of basic hydrogen peroxide (BHP) from depleted BHP solution comprising:
  - a) passing said depleted BHP solution through a first filter assembly to remove solids therefrom,

- b) passing the so-filtered BHP solution through a heat exchanger to cool said solution,
- c) mixing and reacting said solution with  $H_2O_2$  and a reactant selected from the group consisting of  $KO_2$  and  $KOH$ , to regenerate BHP in said solution,
- d) passing the replenished BHP solution through a second filter assembly to remove further solids, each of said filter assemblies having a pair of filters such that the flowing BHP solution is periodically diverted from one to another of said pair of filters so that the nonused filter can be cleaned while said solution passes through the other filter, for continuous filtration of said solution during alternate cleaning of said filters and
- e) passing the so-filtered BHP solution to a collection tank to cool and store same.

**Assignee:** The United States of America as represented by the Secretary of the Air Force  
**Filing Date:** Apr. 11, 1995

**Inventor:** MacKnight, Allen K.; Stancliffe, A. Colin

**Title:** Dry Excited Singlet Delta Oxygen Generator

**Country:** United States

**Patent Number:** 4,342,116

**Issue Date:** Jul. 27, 1982

**Keywords:** Singlet Oxygen Generator (SOG) ; Chemical Oxygen-Iodine Laser (COIL)

**Abstract:** An improved method and apparatus for producing dry excited singlet delta oxygen for use in iodine lasers.

**First Claim:** We claim:

1. A method of producing coherent energy, said method comprising the steps of:
  - providing a flow of inert gas;
  - injecting a liquid mixture of hydrogen peroxide and potassium hydroxide into the flow of said inert gas;
  - interposing a flow of chlorine gas in the path of the liquid flow such that the chlorine, hydrogen peroxide and potassium hydroxide react to produce excited oxygen; and
  - combining the excited oxygen with atomic iodine such that the oxygen acts as an energy transfer agent to pump the  $^2 P_{1/2} - ^2 P_{3/2}$  spin orbit transition of said atomic iodine.

**Assignee:** The Garrett Corp., Los Angeles, CA.

**Filing Date:** Mar. 11, 1980

**Inventor:** McDermott, William E.

**Title:** Singlet Delta Oxygen Generator and Process

**Country:** United States

**Patent Number:** 5,417,928

**Issue Date:** May 23, 1995

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A generator for producing a flow of excited oxygen in the singlet delta electronic state comprising a vacuum chamber, an inlet feed system, an internal reaction zone, a method for cooling said reaction zone, an outlet system for separating the gas from the liquid, and a means for interfacing this device to a lasing device for directing the flowing singlet delta gas into a laser cavity.

**First Claim:** I claim:

1. Apparatus for generating molecular oxygen gas in the electronically excited singlet delta state comprising:
  - (a) a hydrogen peroxide supply reservoir, having a supply-reservoir floor;
  - (b) a hydrogen peroxide collection reservoir, having a collection-reservoir wall;
  - (c) a hollow reaction tube, having a substantially unobstructed central region, extending between said supply reservoir and said collection reservoir, said reaction tube having a supply end and a collection end and a substantially straight-walled inner surface;
  - (d) an injector extending from said supply-reservoir floor into the supply end of said reaction tube and creating a gap between said injector and an interior surface of said supply end;
  - (e) a collector extending from-said collection-reservoir wall into the collection end of said reaction tube and creating a gap between said injector and an interior surface of said collection end.

**Assignee:** Rockwell International Corp., Seal Beach, CA

**Filing Date:** Feb. 25, 1994

**Inventor:** McDermott, William E.; Benard, David J.; Pchelkin, Nicholas R.; Bousek, Ronald R.

**Title:** Continuous Wave Chemically Pumped Atomic Iodine Laser

**Country:** United States

**Patent Number:** 4,267,526

**Issue Date:** May 12, 1981

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** CW laser action achieved on the  $2P_{1/2} - 2P_{3/2}$  transition of the iodine atom by energy transfer from the  $^1\text{DELTA}$ . metastable state of  $\text{O}_2$ . The effluent from a conventional oxygen generator was mixed with molecular iodine at the entrance of a longitudinal flow laser cavity where the  $\text{I}_2$  was dissociated by a small amount of  $\text{O}_2$  ( $^1\text{SIGMA}$ .) that was present in the flow due to energy pooling processes. The measured output power was greater than 4mW.

**First Claim:** What is claimed is:

1. A method for producing a continuous wave, chemically pumped lasing action which comprises:
  - A. providing a resonant cavity having oppositely disposed reflecting means;
  - B. continuously introducing a stream of gaseous molecular oxygen in the singlet-delta electronic state into said cavity;
  - C. admixing a continuous flow of gaseous molecular iodine with said stream of oxygen to form an electronically excited, continuously flowing, gaseous mixture;
  - D. passing said flowing, excited gaseous mixture through said resonant cavity to produce a beam of coherent electromagnetic radiation; and
  - E. continuously exhausting said oxygen and iodine gasses at the end of said resonant cavity subsequent

to

their mixing.

**Assignee:** The United States of America as represented by the Secretary of the Air Force

**Filing Date:** Apr. 13, 1979

**Inventor:** McDermott, William E.; Benard, David J.; Pchelkin, Nicholas R.; Bousek, Ronald R.

**Title:** Gas Generating System for Chemical Lasers

**Country:** United States

**Patent Number:** 4,246,252

**Issue Date:** Jan. 20, 1981

**Abstract:** A method for generating electronically excited oxygen by effecting a chemical reaction between chlorine and basic hydrogen peroxide.

**First Claim:** What is claimed is:

1. A method for preparing molecular oxygen in the excited single-delta electronic state for use as an energizing reactant for chemical lasers which consists essentially of the steps of:
  - (A) introducing a mixture consisting essentially of 200 ml of 90% hydrogen peroxide and 100 ml of sodium hydroxide into the reaction zone of a gas generator;
  - (B) admitting chlorine gas into said reaction-zone and allowing said gas to flow through said hydrogen peroxide mixture at a flow rate of about 100 standard  $\text{cm}^3 \text{sec}^{-1}$  to effect a chemical reaction therebetween;
  - (C) passing the product of said chemical reaction through a low temperature zone to remove water and other high melting point reaction by products; and
  - (D) removing and storing the resulting vibrationally excited oxygen.

**Assignee:** The United States of America as represented by the Secretary of the Air Force

**Filing Date:** April 13, 1979

**Inventor:** McDermott, William E.; Ellis, David E.; Pchelkin, Nicholas R.; Miller, George W.; Benard, David J.; Richardson, Ralph J.

**Title:** Tubular Singlet Delta Oxygen Generator

**Country:** United States

**Patent Number:** 4,558,451

**Issue Date:** Dec. 10, 1985

**Abstract:** A generating device for producing a laser energizing gas in the singlet delta, electronic state comprising a vacuum chamber; a tubular reaction chamber positioned within said vacuum chamber, said reaction chamber having a closed end and an oppositely disposed open end; means positioned in said closed end for introducing a flow of a gaseous reactant into said reaction chamber; means positioned adjacent said closed end at an angle perpendicular to the position of said gas introducing means for introducing a stream of a liquid reactant into said gas flow to effect a chemical reaction there between and the generation of a laser energizing, singlet delta gas; and means for interconnection to a lasing device for directing a flow of said generated, singlet delta gas to a lasing cavity.

**First Claim:** What is claimed is:

1. An apparatus for generating a molecular oxygen gas in the electronically excited singlet delta state consisting essentially of:
  - (A) a housing and means connecting thereto for creating a vacuum there;
  - (B) an elongated tubular reaction chamber positioned within said housing, said reaction chamber having sidewalls running parallel to the longitudinal axis of said reaction chamber and which define a substantially circular cross-sectional interior portion, and said reaction chamber further having a closed end and an oppositely disposed open end;
  - (C) means for introducing and directing a flow of a gaseous reactant into said reaction chamber, said means for introducing said gaseous reactant being positioned within the closed end of said reaction chamber wherein said gaseous reactant flows substantially parallel to the longitudinal axis of said reaction chamber and assumes a substantially circular cross-sectional area as defined by said sidewalls;
  - (D) means for introducing and directing a stream of an aspirated liquid reactant into said reaction chamber adjacent to the flow of said gaseous reactant, said means for introducing a liquid reactant being positioned within the sidewalls of said elongated chamber at an angle perpendicular to the longitudinal axis of said reaction chamber thus providing a gas/liquid interface of circular cross-section along the interior surface of said sidewalls of said chamber to affect a reaction between said gaseous and liquid reactants to generate a singlet delta, electronically excited, molecular oxygen gas; and

(E) said means for creating a vacuum being in fluid communication with said housing at a point adjacent said open end of said reaction chamber thereby directing a flow of said molecular oxygen from said reaction chamber through said housing for subsequent use.

**Assignee:** United States of America as represented by the Secretary of the Air Force

**Filing Date:** Jul. 19, 1982

**Inventor:** Richardson, Ralph J.; Lilienfeld, Harvey V.

**Title:** Process for Generating Singlet-Oxygen

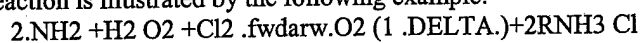
**Country:** United States

**Patent Number:** 4,318,895

**Issue Date:** March 9, 1982

**Keywords:** Basic Hydrogen Peroxide (BHP) with a Nitrogen-Containing Base

**Abstract:** A process and apparatus are provided for producing singlet molecular oxygen, O<sub>2</sub> (1 .DELTA.). A nitrogen containing base such as NH<sub>3</sub>, diethylamine, ethanolamine, propylamine, triethylene diamine, phenethylamine, methyl amine, or dipropylamine is mixed with hydrogen peroxide. Chlorine gas is bubbled through the mixture which reacts therewith to produce singlet molecular oxygen. A preferred embodiment of the reaction is illustrated by the following example:



where RNH<sub>2</sub> is an amine. The apparatus for producing the singlet molecular oxygen is a reactor vessel with the hydrogen peroxide and nitrogen containing base solution as a liquid mixture in the bottom thereof through which chlorine gas is bubbled. The vessel is maintained at a pressure range of 1 to 20 Torr, a temperature range of -30° to 35° C., a pH range of 7 to 12, and the O<sub>2</sub> (1 .DELTA.) is drawn off the vessel through a suitable vent.

**First Claim:** What is claimed is:

1. A process for generating O<sub>2</sub> \* including the steps of:
  - placing H<sub>2</sub>O<sub>2</sub> in a reactor vessel;
  - maintaining the reactor vessel at a pressure of 1 to 20 Torr and a temperature of -30° to 35° C.;
  - maintaining the H<sub>2</sub> O<sub>2</sub> in the reactor vessel at a pH of 7 to 12 with a nitrogen containing base; and
  - bubbling chlorine gas through the H<sub>2</sub> O<sub>2</sub> in the reactor vessel.

**Assignee:** McDonnell Douglas Corporation, Long Beach, CA

**Filing Date:** Nov. 5, 1979

**Inventor:** Rockenfeller, John D.

**Title:** Singlet Delta Oxygen Generator

**Country:** United States

**Patent Number:** 4,461,756

**Issue Date:** Jul. 24, 1984

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A method and apparatus for producing molecular oxygen in the excited singlet delta oxygen electronic state for use as an excited species reactant in a high energy, continuous-wave, chemically pumped laser. In this invention, small amounts of sodium hydroxide and hydrogen peroxide are continuously mixed, reacted, cooled and then combined with chlorine to form a mixture which is injected into a mixing chamber as very fine droplets to provide an efficient means for effecting a reaction which produces excited molecular oxygen.

**First Claim:** What is claimed is:

1. A method for preparing molecular oxygen in the excited singlet delta electronic state for use as an energizing reactant for chemical lasers which comprises the steps of:
  - (a) introducing a flow of hydrogen peroxide and sodium hydroxide reactants into a flowing reactor;
  - (b) mixing the said reactants at a pressure greater than one atm to effect a reaction therebetween and form an intermediate reaction product, and cooling and removing the heat from said reaction at said pressure;
  - (c) passing said intermediate reaction product through a sonic orifice and swirling chamber to form a swirling droplet spray of said intermediate reaction product while simultaneously introducing chlorine into said swirling droplet spray to effect a reaction therebetween and produce excited molecular oxygen;
  - (d) desorbing said excited molecular oxygen in a vacuum chamber downstream of the said sonic orifice and swirling chamber;
  - (e) removing any entrained liquid water droplets and water vapor from said excited molecular oxygen; and
  - (f) removing and storing the resulting excited molecular oxygen.

**Assignee:** The United States of America as represented by the Secretary of the Air Force  
**Filing Date:** Sep. 30, 1982

**Inventor:** Schall, Wolfgang

**Title:** Oxygen-iodine laser

**Country:** United States

**Patent Number:** 5,802,095

**Issue Date:** Sep. 1, 1998

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** In order to improve an oxygen-iodine laser comprising a reaction unit for the generation of a gas stream composed of excited oxygen by chemical reaction between a reaction liquid and a reaction gas, a steam trap with a condensation chamber, in which steam entrained by the gas stream is condensed onto cold surfaces, an iodine injector, which injects iodine into the gas stream to generate a laser-active gas mixture, and a laser resonator with the laser-active gas mixture flowing through it, in such a way as to obtain a gas stream as free from steam as possible using the simplest possible means, it is proposed that the cold surfaces for separation of the steam are formed by liquid surfaces of a condensation liquid moved in the condensation chamber.

**First Claim:** What is claimed is:

1. An oxygen-iodine laser having a laser resonator with a laser-active gas mixture of excited oxygen and iodine flowing therethrough, comprising:

a reaction unit in which a chemical reaction between a reaction liquid and a reaction gas occurs to generate a gas stream comprising excited oxygen and entrained steam;  
 a steam trap with a condensation chamber through which the gas stream flows;  
 said steam trap comprising cold surfaces for separating the steam from the gas stream by condensation; said cold surfaces being formed by surfaces of a condensation liquid moving in the condensation chamber; and an iodine injector which injects iodine into the gas stream to generate the laser-active gas mixture.

**Assignee:** Deutsche Forschungsanstalt Fuer Luft-und Raumfahrt e.V., Germany  
**Filing Date:** Jun. 13, 1996

**Inventor:** Stelman, David

**Title:** Elimination of Anomalous Freezing of Basic Hydrogen Peroxide in the Chemical Oxygen Iodine Laser

**Country:** United States

**Patent Number:** 6,224,786

**Issue Date:** May 1, 2001

**Keywords:** Basic Hydrogen Peroxide (BHP)

**Abstract:** A basic hydrogen peroxide composition is described, wherein the basic hydrogen peroxide is formed by mixing aqueous potassium hydroxide and aqueous hydrogen peroxide in a mole ratio such that the resulting basic hydrogen peroxide composition does not crystallize when maintained at a temperature down to  $-21^{\circ}\text{C}$ . The basic hydrogen peroxide composition is especially suitable for use with chemical oxygen iodine laser systems. The mole ratio of hydrogen peroxide to potassium hydroxide corresponds to a composition represented by at least one location within a triangular region on a triangular phase diagram which is substantially bounded by the shortest line having coordinates (26.4, 16.0, 57.6), (62.3, 37.7, 0.0), and (46.8, 53.2, 0.0), wherein these coordinates correspond to the respective weight percentages of potassium hydroxide, hydrogen peroxide and water.

**First Claim:** What is claimed is:

1. A basic hydrogen peroxide composition, wherein the basic hydrogen peroxide is formed by mixing aqueous potassium hydroxide and aqueous hydrogen peroxide in a mole ratio such that the resulting basic hydrogen peroxide composition does not crystallize when maintained at a temperature down to  $-21^{\circ}\text{C}$ .

**Assignee:** The Boeing Company

**Filing Date:** Nov. 16, 1999

**Inventor:** Thayer, William J., III

**Title:** Uniform Droplet Generator

**Country:** United States

**Patent Number:** 5,392,988

**Issue Date:** Feb. 28, 1995

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** The uniform droplet injector assembly is a rigid, low mass injector having a plurality of nozzles therein attached to a manifold. The manifold vibrates by piezoelectric actuators and springs in combination. The droplet injector array allows the process stream to flow through the injector assembly with the droplets uniformly dispersed into this stream. The moving parts such as the injector assembly, springs, and actuators are structurally resonant at a frequency near the droplet formation frequency. The colinear, spring/actuator configuration minimizes internal stresses due to manufacturing tolerances, preloading requirements, temperature changes, and cyclic operation in a large area generator. The linear spring/actuator configuration has low stiffness in the vibration direction and high stiffness in transverse direction to eliminate motions which would cause nonuniformly sized droplets.

**First Claim:** What is claimed is:

1. A droplet injector assembly, said droplet injector assembly comprising:

an injector array, said injector array comprising:

a plurality of injector tubes, said injector tubes being parallel to one another, said injector tubes having a plurality

of nozzles therein for outputting streams of droplets of a fluid, said nozzles being in a single row in each tube,

said plurality of injector tubes being located in an upstream group and a downstream group, said injector tubes

in said groups alternating in position so as to present a uniform array to a process stream flowing thereby;

a supply manifold, said supply manifold receiving said fluid from a fluid source external to said droplet assembly,

said injector tubes connected into said supply manifold;

means for vibrating, said means for vibrating connected to said injector said vibrating means causing said streams

of said fluid to break into streams of droplets of a predetermined size; and

means for mounting, said means for mounting connected to said means for vibrating and said injector array, said

means for mounting being connected into a flow channel having therein a process stream that flows through said

injector assembly.

**Assignee:** The United States of America as represented by the Secretary of the Air Force, Washington, DC

**Filing Date:** Jan. 19, 1994

**Inventor:** Thayer, William J., III

**Title:** Transverse Flow Uniform Droplet O<sub>2</sub> (<sup>1</sup>.DELTA.) Generator and Method for its Use.

**Country:** United States

**Patent Number:** 5,658,535

**Issue Date:** Aug. 19, 1997

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A transverse flow uniform droplet generator and method for its use. The droplet generator, such as is used with a gas laser system, produces singlet oxygen from a flow of droplets of liquid basic hydrogen peroxide (BHP) reacting with a transverse a flow of He/Cl<sub>2</sub> gas mixture. The resulting flow of singlet oxygen travels in the same direction as the He/Cl<sub>2</sub> gas mixture and the unreacted BHP is collected on the opposite of the reaction volume from which it enters. Very uniformly-size BEP droplets are formed by an injector which specific mechanical resonance characteristics and the flow of the BHP and the gas mixture in the generator volume is also carefully controlled.

**First Claim:** I claim:

1. An apparatus to promote a chemical reaction between a chlorine-bearing gas stream and a liquid basic hydrogen peroxide stream, comprising:

a flow device to produce a continuous substantially linear flow of the chlorine-bearing gas stream, the substantially linear flow of the chlorine-bearing gas stream being directed in a first direction through a chemical reaction volume; and an injector to generate a discrete substantially linear flow of the liquid basic hydrogen peroxide stream, the substantially linear flow of the liquid basic hydrogen peroxide stream occurring in a second direction that is substantially perpendicular to the first direction and directed through the chemical reaction volume, whereby the chlorine-bearing gas stream and the liquid basic hydrogen peroxide stream react chemically to produce a substantially linear flow of singlet oxygen.

**Assignee:** STI Optronics Corp., Bellevue, WA

**Filing Date:** Jul. 14, 1995

**Inventor:** Uchiyama, Taro; Takehisa, Kiwamu; Ishizaki, Isao

**Title:** System for Generation of Singlet-Delta Oxygen

**Country:** United States

**Patent Number:** 4,643,889

**Issue Date:** Feb. 17, 1987

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A process for generating an excited molecular oxygen by a procedure which comprises causing a mixture of an alkaline aqueous solution with hydrogen peroxide to wet the surface portion of a layer of a hydrophilic and gas-pervious material, causing a molecular chlorine-containing gas to penetrate said layer from the side opposite said surface thereof, enabling said gas during the penetration thereof through said material to react with said mixed aqueous solution which has wetted said surface portion of said material, and thereby inducing generation of said excited molecular oxygen,  $O_2$  (1 .DELTA.), through said surface portion of said layer wetted by said mixed aqueous solution.

**First Claim:** What is claimed is:

1. A process for generating an excited molecular oxygen by a procedure which comprises causing a mixture of an alkaline aqueous solution with hydrogen peroxide to wet the surface portion of a layer of a hydrophilic and gas-pervious material, causing a molecular chlorine-containing gas to penetrate said layer from the side opposite said surface thereof, enabling said gas during the penetration thereof through said material to react with said mixed aqueous solution which has wetted said surface portion of said material, and thereby inducing generation of said excited molecular oxygen,  $O_2$  (1.DELTA.), through said surface portion of said layer wetted by said mixed aqueous solution.

**Assignee:** Mitsui Grinding Wheel Co., Ltd., Saitama, Japan

Uchiyama, Taro

**Filing Date:** Mar. 31, 1986

**Inventor:** Vetrovec, Jan

**Title:** Method of Operating Electrolytic Cell to Produce Highly Concentrated Alkaline Hydrogen Peroxide.

**Country:** United States

**Patent Number:** 6,004,449

**Issue Date:** Dec. 21, 1999

**Keywords:** Basic Hydrogen Peroxide (BHP)

**Abstract:** An alkaline peroxide cell for electrolytic regeneration of spent BHP from a chemical oxygen iodine laser, the cell having a for regenerating chlorine and a peroxide cell for regenerating BHP. The chlorine compartment having a potassium chloride electrolyte and producing chlorine gas for the chemical oxygen iodine laser. The peroxide cell having a spent BHP electrolyte and producing BHP for the chemical oxygen iodine laser. A cation exchange membrane between the chlorine compartment and the peroxide compartment allows potassium ions to be transported from the chlorine compartment to the peroxide compartment.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. A process for the manufacture of an aqueous solution of basic hydrogen peroxide by cathodic reduction of oxygen in the presence of alkaline electrolyte in an electrolytic cell; said cell comprising an anode; a liquid permeable diaphragm; and a porous, packed bed, self-draining cathode; wherein said cathode is in contact with a current distributor on one face of said cathode and

- is in contact with said liquid permeable diaphragm on an opposite face of said cathode;  
 wherein said cathode comprises a bed of sintered particles or an agglomeration of loose particles and said cathode has pores of sufficient size and number to allow both gas and liquid to flow therethrough;  
 wherein said particles are graphite chips coated with a mixture of carbon black and polytetrafluorethylene;  
 wherein said pores form pasageways having minimum diameter of 30 to 50 microns;  
 wherein said current distributor is made of high purity nickel or suitable nickel alloy;  
 wherein said liquid permeable diaphragm comprises 2 to about 5 layers of
- (A) a microporous polyolefin film or
  - (B) a composite comprising said microporous polyolefin film and a support fabric resistant to deterioration upon exposure to electrolyte and electrolysis products thereof;
- wherein said microporous polyolefin film of the liquid permeable diaphragm is characterized as hydrophilic and having porosity of about 38% to about 45%, an effective pore size of about 0.02 to about 0.04 micrometers, and a thickness of about 1 mil;  
 wherein said electrolyte flowed into the cathode is a an aqueous solution of potassium hydroxide with a concentration of at least 1.5 mol/liter;  
 wherein said electrolyte is supplied to the said cathode with 3-10 inches hydraulic head, said head measured from the top of said electrolyte in the cell;  
 wherein the cathode has means to receive gas reactant;  
 wherein said gas flowed into said cathode is oxygen or is an oxygen carrying gas;  
 wherein said said process comprising:
- (A) flowing said electrolyte between said anode and said diaphragm;
  - (B) electrolytically reacting said electrolyte to generate oxygen gas on said anode surface;
  - (C) allowing said oxygen gas generated on said anode to be removed by the flow of said electrolyte flowing past said anode;
  - (D) allowing portion of the said electrolyte flowed in proximity of said anode to flow through said liquid permeable diaphragm into said cathode;
  - (E) flowing oxygen into a portion of said self-draining cathode;
  - (F) controllably flowing a liquid electrolyte through said liquid permeable diaphragm into a portion of said porous, packed bed, self-draining cathode at a rate about equal to the drainage of the cathode, such that said electrolyte flowrate through said diaphragm is about 0.04 to about 0.80 milliliters per minute per square inch of diaphragm area;
  - (G) electrolytically reacting said liquid electrolyte within said cathode with said gas to form peroxy and hydroxyl anions in said electrolyte;
  - (H) removing the products of electrolysis from said self-draining cathode;
  - (I) drawing an electric current between said anode and said cathode with the current density on said cathode being at least 0.6 amperes per square inch;
  - (J) maintaining the temperature of said cell and said electrolyte in the range of about -5 degrees Centigrade to about +25 degrees Centigrade.

**Assignee:** Boeing North American, Inc., Seal Beach, CA

**Filing Date:** Feb. 9, 1998

**Inventor:** Vetrovec, Jan

**Title:** Chemical Oxygen-Iodine Laser (COIL)/Cryosorption Vacuum Pump System

**Country:** United States

**Patent Number:** 6,154,478

**Issue Date:** Nov. 28, 2000

**Keywords:** Chemical Oxygen-Iodine Laser (COIL); Vacuum Pump System

**Abstract:** A high-capacity cryosorption vacuum pump system for a light-weight and compact chemical oxygen-iodine laser. The cryosorption vacuum pump system included a gas chiller and a bed of zeolite or other suitable sorption material. Gas exhausted from the chemical oxygeniodine laser is first chilled to about 100 degrees Kelvin and the condensable gases are removed. Cold and dry gas is then adsorbed onto a bed zeolite cooled to a temperature of approximately 80 degrees Kelvin. The zeolite bed uses a suitable zeolite material preferably in a granulated form and configured in layers several millimeters to several centimeters thick to provide an exposed surface of suitable size. The zeolite is enclosed in a suitable vacuum vessel and thermally insulated. Chilling of the zeolite is accomplished by a contact with suitable cryocooled surfaces or by exposing the zeolite to a cold light noble gas. When the sorption capacity of the zeolite is exhausted, the cryosorption vacuum pump can be regenerated by allowing the zeolite and the gas chiller to warm up and liberate gas. Regeneration can be expedited by heating the zeolite and the gas chiller with electric heaters, by flowing warm dry gas through the zeolite bed or exposing the zeolite to electromagnetic radiation. Gas liberated in the regeneration process is removed from the vacuum vessel by a suitable vacuum pump. The cryosorption vacuum pump system is a compact light-weight system which provides effective vacuum pumping for the chemical laser. In addition, the cryosorption vacuum pump safely contains all of the laser exhaust gas, thereby eliminating concerns over thermal signature, visible clouds of steam, excessive noise level, or safety hazards associated with laser gas exhausted into atmosphere.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. A Chemical Oxygen-Iodine Laser (COIL)/cryosorption vacuum pump system comprising:
  - (a) a COIL including a laser cavity; and,
  - (b) a cryosorption vacuum pump system for removing exhaust gases from said laser cavity at a rate and sufficiently low pressure to sustain lasing action, said cryosorption vacuum pump system, comprising:
    - (i) a gas chiller assembly for chilling a flow of laser gases received from said laser cavity, said gas chiller removing condensable vapors therefrom, said condensable vapors including water and iodine, said gas chiller providing cold dry laser gases;
    - (ii) a cryosorption assembly including a bed of cryosorption material for receiving and absorbing said cold dry laser gases from said gas chiller;
    - (iii) means associated with said gas chiller assembly for refrigerating said gas chiller assembly;
    - (iv) means associated with said cryosorption assembly for refrigerating said bed of cryosorption material; and
    - (v) means for regenerating said gas chiller assembly and said cryosorption assembly by removing the condensable vapors and laser gases therefrom.

**Assignee:** The Boeing Company, Seal Beach, CA

**Filing Date:** Jun. 30, 1998

**Inventor:** Wagner, Ross I.

**Title:** Singlet Delta Oxygen Generator and Process

**Country:** United States

**Patent Number:** 4,310,502

**Issue Date:** Jan. 12, 1982

**Keywords:** Singlet Oxygen Generator (SOG)

**Abstract:** A singlet delta oxygen generator 10 comprises a static or motionless mixer 12 having a gas inlet 14 through which chlorine gas reactant is introduced into the static mixer and a liquid inlet 16 through which the basic sodium hydroxide/hydrogen peroxide solution is introduced. As the reactants pass through static mixer 12, the gaseous products and liquid by-products are formed. The product stream passes through liquid/gas separator 26 wherein the liquid by-product stream is diverted to sump 28 and the gaseous product stream is conveyed to a low volume trap 30. The temperature of trap 30 is maintained at approximately  $-80^{\circ}$  C. so as to solidify and thereby remove any water or hydrogen peroxide vapor which might remain in the product stream. From the low volume trap 30, the product stream is then conveyed to chlorine trap 34 wherein any excess chlorine gas present in the system is retained.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. A singlet delta oxygen generator, comprises:

- a static mixer having a liquid inlet, a gas inlet, a plurality of left and right-hand helical mixing elements, arranged in alternating sequence, and a product exit zone;
- a liquid gas separator, oriented across said exit zone of said static mixer so that said liquid may be transferred through said separator while the gaseous product stream is diverted away from said liquid by-product; and
- a low-volume trap for freezing water and hydrogen peroxide vapor contained in said gaseous product stream.

**Assignee:** Rockwell International Corp., El Segundo, CA

**Filing Date:** May 29, 1980

## U.S. Patents Dealing with COIL based on the Chlorine-BHP Reaction

- Beshore and Ullman, 1997, Fast Response Iodine Vaporization with an Integrated Atomizer and Mixer, 5,693,267
- Davis, Lilienfeld, 1987, Chemical Oxygen-Iodine Laser, 4,653,062
- Dickerson, 1988, Chemical Oxygen Iodine Laser, Rockwell International Corp., El Segundo, CA, 4,780,880
- Florentino, Gupta, 1999, Gain Generator for High-Energy Chemical Lasers, 5,870,422
- Hartlove, Clendening, 1999, High Energy Airborne Coil Laser, 5,974,072
- Jensen, 1993, Method and Apparatus for Determining the Concentration of Oxygen, 5,242,835
- Schmiedberger, Kodymova, 1993, Modulation of Oxygen-Iodine Laser, 5,199,041
- Wagner, 1988, Chemical Laser System Employing Iodine Atoms as a Lasing System, 4,787,091.

**Reference Type:** US Patent

**Record Number:** 1

**Inventor:** Beshore, David G.; Ullman, Alan Z.

**Year:** 1997

**Title:** Fast Response Iodine Vaporization with an Integrated Atomizer and Mixer

**Country:** United States

**Patent Number:** 5,693,267

**Issue Date:** Dec. 2, 1997

**Keywords:** Chemical Oxygen-Iodine Laser (COIL); Iodine Flow Control

**Abstract:** This invention provides a means of achieving the close control of iodine flow rate, temperature of the resulting combined gaseous mixture of iodine in diluent gas, as well as the rapid start and stop response time needed for full-scale laser operation. It comprises an iodine charge stored as a solid and is heated to convert the iodine to a liquid, a means to heat the iodine under pressure to extend the liquid temperature range of iodine, an atomizer for complete vaporization of the iodine, a helium iodine mixer to provide heat for iodine vaporization purporting iodine to helium proportion mass ratio and provides for complete mixing and a flow control system which controls the low iodine flow rates accurately.

**First Claim:** What is claimed and desired to be secured by Letters Patent of the United States is:

1. An iodine vaporizer comprising:
  - a mixing chamber for mixing atomized iodine and helium to form helium-iodine droplets,
  - a vessel for storing an iodine charge as a solid,
  - a means to heat the solid iodine charge under pressure in the vessel to convert the solid iodine to a liquid and extend the liquid temperature range of the liquid iodine,
  - an iodine atomizer in the mixing chamber fluidly connected to the vessel to feed atomized iodine droplets to the mixing chamber,
  - a helium manifold for injecting helium into the mixing chamber,
  - a means for heating the mixing chamber to promote the mixing of helium with atomized iodine and to keep the iodine vaporized,
  - a means for controlling the flow of iodine to the iodine atomizer. such that a supply of helium-iodine droplets having a mass ratio of between 0.5 and 2 to 1 is produced.

**Assignee:** Boeing North American, Inc., Seal Beach, CA

**Filing Date:** Sep. 27, 1996

**Inventor:** Davis, Steven J.; Lilienfeld, Harvey V.; Neumann, David K.; Whitefield, Phillip D.

**Year:** 1987

**Title:** Chemical Oxygen-Iodine Laser.

**Country:** United States

**Patent Number:** 4,653,062

**Issue Date:** Mar 24, 1987

**Keywords:** Chemical oxygen-iodine laser (COIL)

**Abstract:** An oxygen-iodine laser system that includes a source of gaseous singlet delta oxygen  $O_2$  ( $^1\text{DELTA}$ .) and a source of gaseous iodine monochloride, ICl, that directs their respective gases to manifolds and then to a mixing reacting nozzle. The nozzle discharges the mixed gases into a lasing cavity. When mixed the ICl dissociates into atomic iodine, I, and atomic chlorine, Cl, in the presence of the excited oxygen. The atomic iodine is subsequently excited to  $I(^2p_{1/2})$  lasing state by the excited oxygen. The lasing cavity, which includes optical means for extracting radiation, includes exhaust ports connected to an exhaust system. The advantage of using ICl in the laser rather than conventional source of atomic iodine is that for a given temperature the operating pressure of the laser can be higher without encountering efficiency reducing condensation of the iodine.

**First Claim:** We claim:

1. A chemical oxygen-iodine laser system for producing a beam of high energy coherent radiation comprising:

a singlet molecular oxygen generating means for producing a gaseous flow of oxygen molecules in an excited state,

an iodine monochloride generating means for producing a gaseous flow of iodine monochloride,

mixing nozzles means for receiving gaseous reactants and discharging these reactants in a mixing flow,

a singlet oxygen manifold means connected by conduit means to said singlet oxygen generating means and to said mixing nozzle means for providing a flow of gaseous singlet oxygen to said mixing nozzle means,

an iodine monochloride manifold means connected to said iodine monochloride generating means and to said mixing nozzle means for providing a flow of gaseous iodine monochloride to said mixing nozzle means,

laser cavity means formed by a sealed enclosure means connected to said mixing nozzle means for receiving flow of gaseous singlet oxygen and iodine monochloride from said mixing nozzle means, whereby iodine monochloride reactants with singlet oxygen to form atomic chlorine and atomic iodine and the atomic iodine formed subsequently reacts with singlet oxygen to raise the atomic iodine to a lasing state and permit the extraction of a laser beam from said laser cavity means, and exhaust manifold means connected to said laser cavity for extracting the reactants from said laser cavity.

**Assignee:** The United States of America as represented by the Secretary of the Air Force

**Filing Date:** Jun. 18, 1985

**Inventor:** Dickerson, Robert A.

**Title:** Chemical Oxygen Iodine Laser

**Country:** United States

**Patent Number:** 4,780,880

**Issue Date:** Oct. 25, 1988

**Keywords:** Chemical oxygen-iodine laser (COIL)

**Abstract:** A method for enhancing the lasing action in a chemical oxygen iodine laser wherein a gas stream having a desired reactant gas concentration profile is combined with a diluent gas concentration profile using hydrogen as the diluent gas.

**First Claim:**

What is claimed and desired to be secured by Letters Patent of the United States is:

1. In a method for converting infrared laser radiation to visible laser radiation comprising the steps of injecting a mixture of iodine, oxygen and fluorine gases into a laser cavity and passing infrared laser radiation having a wavelength of 1315 nm through the gases in said cavity to excite molecules therein and cause reactions among the molecules resulting in the production of excited iodine monofluoride molecules which release their excitation energy to produce visible laser radiation, wherein the improvement comprises:

diluting the reactive gases with hydrogen gas in stoichiometric proportions;  
forming exhaust gases;  
cooling said exhaust gases to form water vapor by condensation; and  
exhausting said condensed water vapor into a cold trap thereby eliminating exhaust pumps in the laser operation.

**Assignee:** Rockwell International Corp., El Segundo, CA

**Filing Date:** May 14, 1987

**Inventor:** Florentino, Caesar C.; Gupta, Raj K.; Hartlove, Jeffrey S.; Clendening, Charles W., Jr.; Reeve, James L.

**Title:** Gain Generator for High-Energy Chemical Lasers

**Country:** United States

**Patent Number:** 5,870,422

**Issue Date:** Feb. 9, 1999

**Keywords:** Chemical oxygen-iodine laser (COIL)

**Abstract:** A gain generator 10 for use in high-energy flowing gas lasers such as COIL devices comprises a chemical reactant mixing nozzle 12 disposed in a gain medium 16. The nozzle includes a plurality of blades 22 formed of a plastic material resistant to chemical attack at the operating temperature of the gain medium and non-catalytic to O<sub>2</sub> (<sup>1</sup>DELTA.). A preferred material is polyetherimide. The gain medium includes octagonal shaped openings 50 for the optical mode of the laser beam.

**First Claim:** What is claimed is:

1. A chemical reactant mixing nozzle for use in the gain generator of a high-energy chemical laser to generate photons, the nozzle comprising:

- a) a plurality of blades comprised of a plastic material;
- b) a plurality of nozzle passages extending through the nozzle between adjacent pairs of the blades; and
- c) a plurality of holes formed in each blade in communication with at least one of the nozzle passages;

wherein the plastic material is (i) resistant to chemical attack by chemical species that contact the blades at the operating temperature of the nozzle, and (ii) has a service temperature greater than about the operating temperature of the nozzle.

**Assignee:** TRW, Inc., Redondo Beach, CA

**Filing Date:** Jul. 9, 1997

**Inventor:** Hartlove, Jeffrey S.; Clendening, Charles W., Jr.; Day, Robert J.; Koop, Gary C.

**Title:** High Energy Airborne Coil Laser

**Country:** United States

**Patent Number:** 5,974,072

**Issue Date:** Oct. 26, 1999

**Keywords:** Chemical oxygen-iodine laser (COIL)

**Abstract:** A high energy chemical laser capable of being operated in an aircraft to interdict and destroy theater ballistic missiles is provided. A key to the chemical laser of the invention is the use of individual chemical lasers whose individual photon energy outputs can be combined into a single high-energy laser beam.

**First Claim:** what is claimed is:

1. A high power chemical laser suitable for use in an airborne anti-theater ballistic missile system, the chemical laser being a COIL comprising a bank of two or more individual photon generating modules, each module having a distinct photon generating chamber, wherein all of the photon generating chambers are optically connected so that the total photon output of the chemical laser is the sum of the photon outputs from each of the photon generating modules.

**Assignee:** TRW Inc., Redondo Beach, CA

**Filing Date:** Jan 20, 1998

**Inventor:** Jensen, Niels-Henrik

**Title:** Method and Apparatus for Determining the Concentration of Oxygen

**Country:** United States

**Patent Number:** 5,242,835

**Issue Date:** Sep. 7, 1993

**Keywords:** Chemical oxygen-iodine laser (COIL)

**Abstract:** The concentration of molecular oxygen in a sample is determined by exciting oxygen molecules of the sample from the electronic ground state to the excited  $^1\text{DELTA}_g$  state (excited singlet state), measuring a 1270-nm luminescence characteristic of the excited oxygen molecules (singlet oxygen) and correlating the luminescence characteristic measured with the concentration of molecular oxygen in the sample. Normally, the 1270-nm luminescence characteristic is the 1270-nm luminescence intensity. Preferably, the oxygen molecules are excited by being subjected to diffusion contact with a sensitizer such as a porphyrin or a porphyrin-related compound, e.g. a transition metal complex of a porphyrin. The sensitizer is brought an oxygen-exciting electronic state by absorption of electromagnetic radiation such as light, the oxygen-exciting electronic state optionally being adapted to the measuring system employed by means of a quencher such as a substituted polyene. The sensitizer may be present in an organic solvent or a polymer such as polyvinylchloride. The oxygen-containing sample is preferably a sample of biological origin such as a blood sample.

**First Claim:** I claim:

1. A method of determining the concentration of ground state molecular oxygen in a test sample, said method comprising:
  - (a) exciting oxygen molecules of the test sample from the electronic ground state to the excited  $^1\text{DELTA}_g$  state (excited singlet state),
  - (b) measuring a 1270-nm luminescence characteristic of the excited oxygen molecules in the test sample,
  - (c) quantitatively correlating the measured 1270-nm luminescence characteristic with standard values determined on the basis of a positive quantitative correlation between (i) 1270-nm luminescence signals of excited oxygen molecules in reference samples having known, pre-selected concentrations of ground state molecular oxygen and (ii) the concentrations of ground state molecular oxygen in the reference samples, and
  - (d) quantifying the content of ground state molecular oxygen in the test sample on the basis of the quantitative correlation of the measured 1270-nm luminescence characteristic with the standard values.

**Assignee:** Radiometer A.S, Copenhagen, Denmark

**Filing Date:** Jul. 21, 1992

**Inventor:** Schmiedberger, Josef; Kodymova, Jarmila; Kovar, Jiri; Spalek, Otomar; Trenda, Pavel

**Title:** Modulation of Oxygen-Iodine Laser

**Country:** United States

**Patent Number:** 5,199,041

**Issue Date:** Mar. 30, 1993

**Keywords:** Chemical oxygen-iodine laser (COIL)

**Abstract:** A method of modulating an oxygen-iodine laser comprises applying an external magnetic field having an intensity of up to 800 A.cm-1 to the active zone of the laser and, at the same time, changing the magnetic field intensity to change the output power of the laser.

**First Claim:** We claim:

1. A method of modulating a continuously pumped chemical oxygen-iodine laser having a body containing an optical resonator and a laser active zone in the resonator where oxygen and iodine react to generate laser light, comprising:

generating a magnetic field of intensity up to 800 A.cm-1, externally of the body, the magnetic field extending into the laser active zone, and varying the intensity of the magnetic field according to a selected timing for modulating an output power of laser light from the optical resonator according to the selected timing.

**Assignee:** Ceskoslovenka Akademie Ved

**Filing Date:** Jul. 12, 1991

**Inventor:** Wagner, Ross I.

**Title:** Chemical Laser System Employing Iodine Atoms as a Lasing System

**Country:** United States

**Patent Number:** 4,787,091

**Issue Date:** Nov. 22, 1988

**Keywords:** Chemical oxygen-iodine laser (COIL)

**Abstract:** A chemical iodine laser system 10 is provided with a reactive iodine producing container (12) for housing a reactive iodine generating composition. Singlet delta oxygen produced by oxygen generator (30) is mixed with iodine atoms and conveyed to a laser cavity.

**First Claim:** Having thus described a preferred embodiment of my invention, that which I claim is new and desired to secure by Letters Patent of the United States is:

1. A chemical oxygen/iodine transfer laser system including an apparatus for chemical generation of gaseous iodine comprising:

- (a) means for conveying gaseous iodine from an iodine generating apparatus to a mixing venturi said generating apparatus comprising: (1) a reactive iodine producing container; (2) a reactive iodine generating composition including a combustible fuel and an oxidizer retained within the container; and (3) an electronic squib igniter means for effecting a chemical reaction, of the reactive iodine generating composition within the container
- (b) means for producing and conveying an excited energizing gas to a mixing venturi to be mixed and reacted with gaseous iodine;
- (c) a laser cavity; and
- (d) means for conveying mixed and reacted iodine atoms and excited energized gas to the laser cavity.

**Assignee:** Rockwell International Corp., El Segundo, CA

**Filing Date:** Jul. 13, 1987

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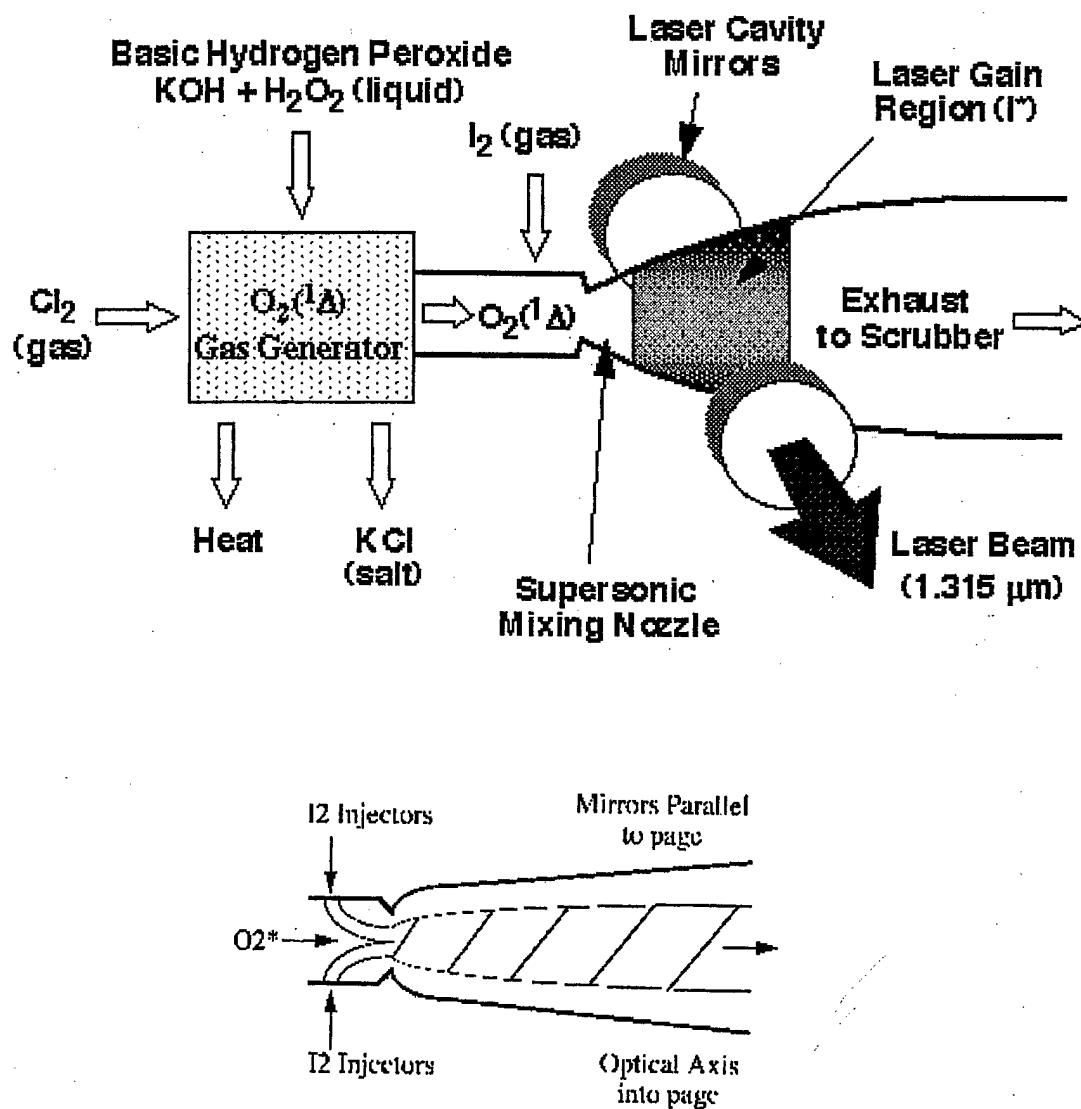
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● Primary COIL reactions:

- »  $I_2 + O_2^* \rightarrow I_2^* + O_2$
- »  $I_2^* + O_2^* \rightarrow 2I + O_2$
- »  $I + O_2^* \rightarrow I^* + O_2$
- »  $I^* \rightarrow I + h\nu$  (i.e., a photon is emitted)
- » (\* denotes an excited molecular or atomic state)

Figure 1. Schematic of COIL and Primary COIL Reactions  
([www.staff.uiuc.edu/~carroll/coil.html](http://www.staff.uiuc.edu/~carroll/coil.html), 1996)

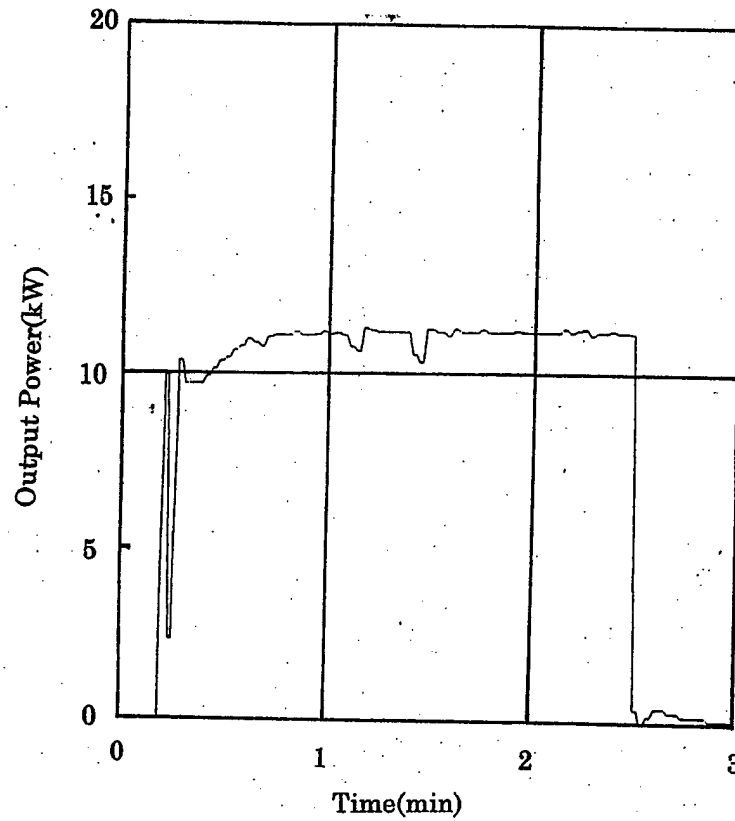


Figure 2. Performance Data of a 10-kW Supersonic COIL (Naito et al. 1997)

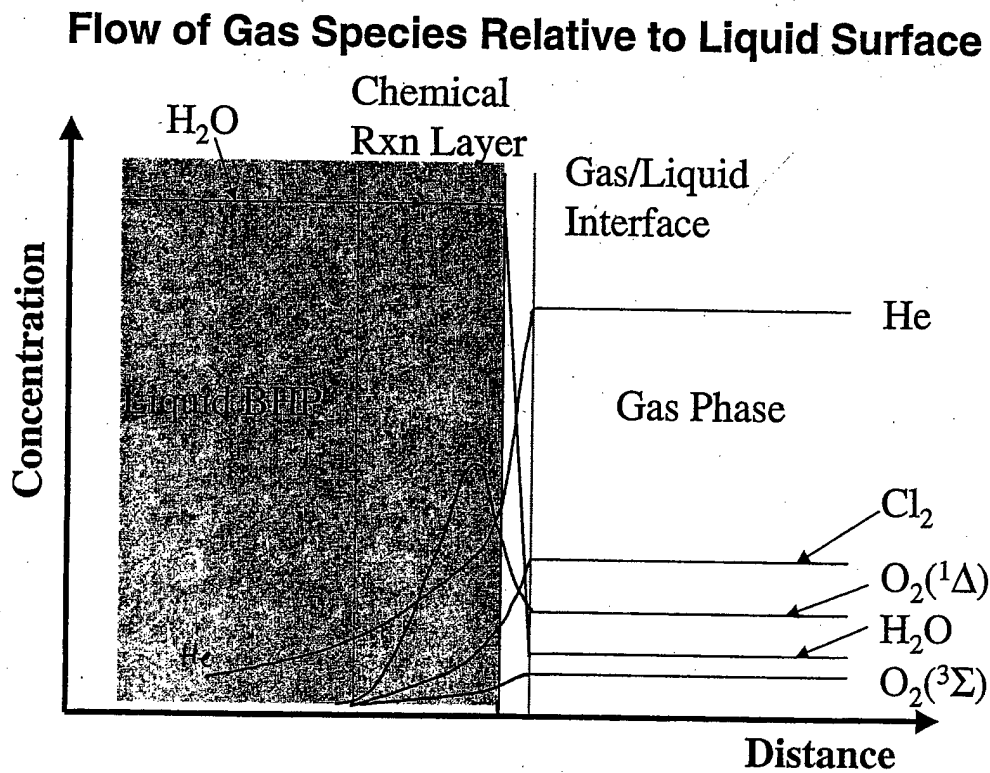
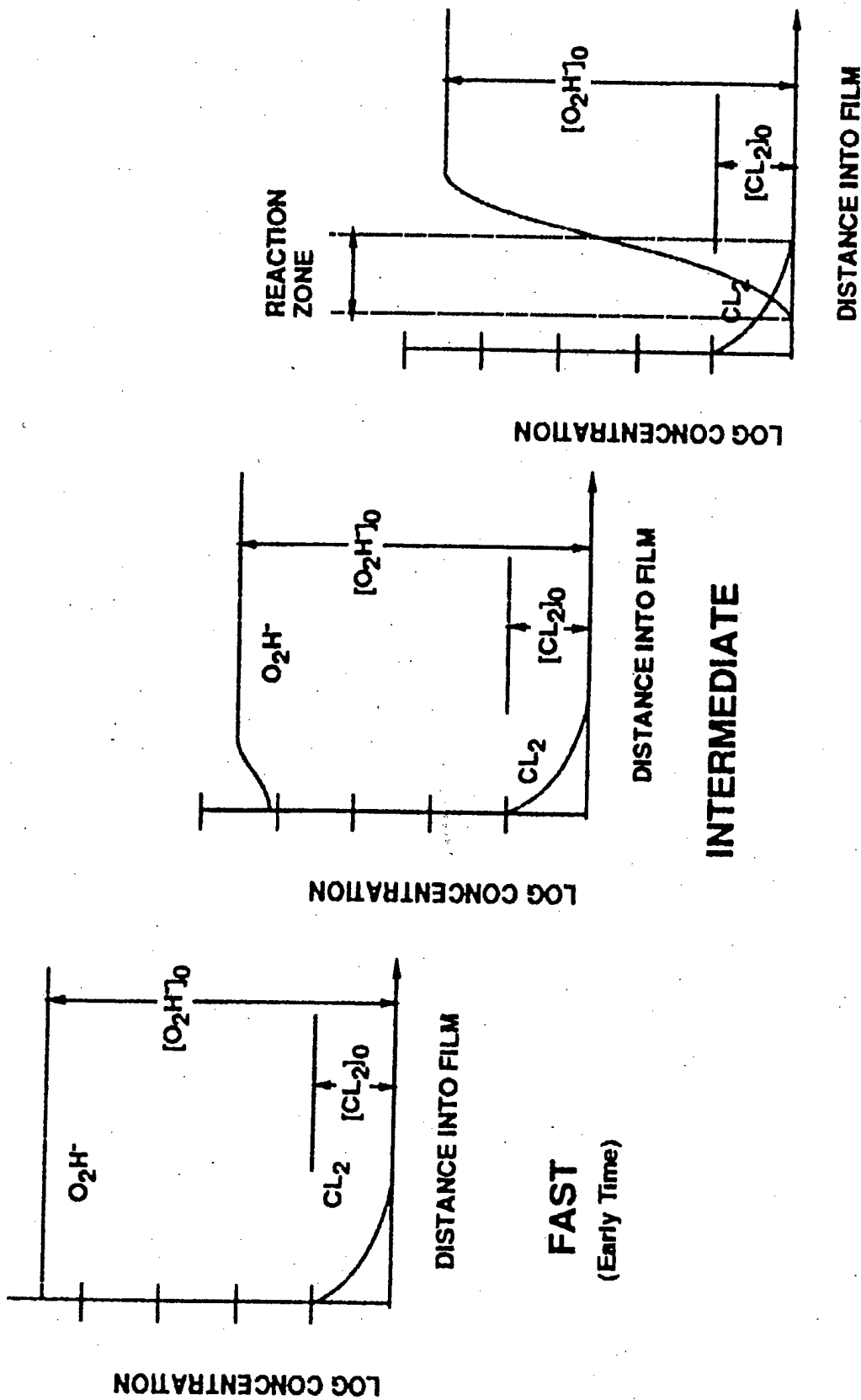


Figure 3. Species Concentrations at the Chlorine-BHP Reaction Interface (Thayer III, 1992)



**FROM: TRANSPORT PHENOMENA,  
BIRD, STEWART & LIGHTFOOT**

**INSTANTANEOUS  
(Late Time)**

**INTERMEDIATE**

**FAST  
(Early Time)**

**INFINITE RATE WHEN REACTION ZONE  $\rightarrow$  0 THICKNESS**

Figure 4. Predicted Rates of Chlorine-BHP Reaction at Different Stages (McDermott, 1992)

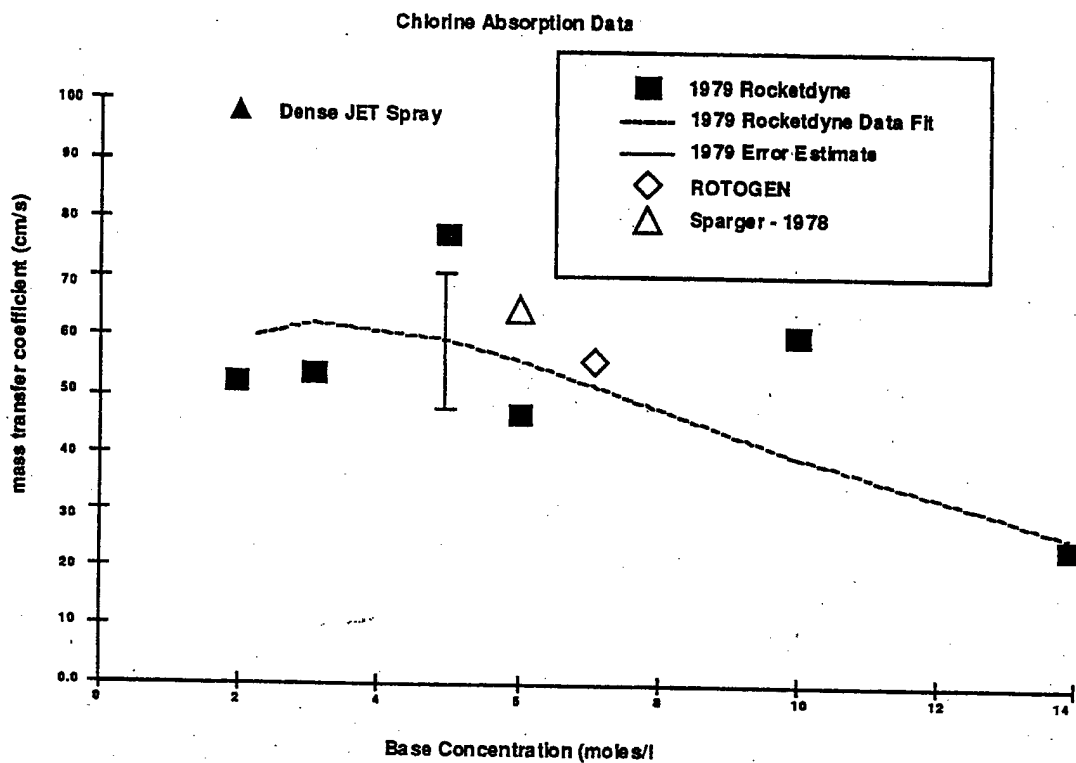


Figure 5. Measured Chlorine Mass-Transfer Rates (McDermott, 1992)

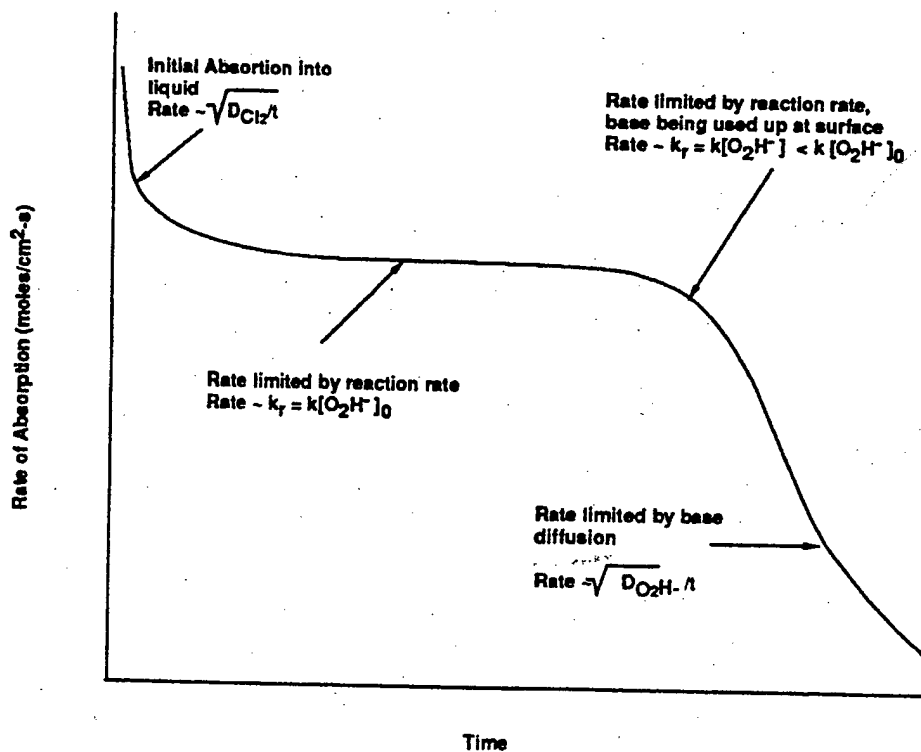


Figure 6. Rate of Chlorine Absorption as a Function of Time (McDermott, 1992)

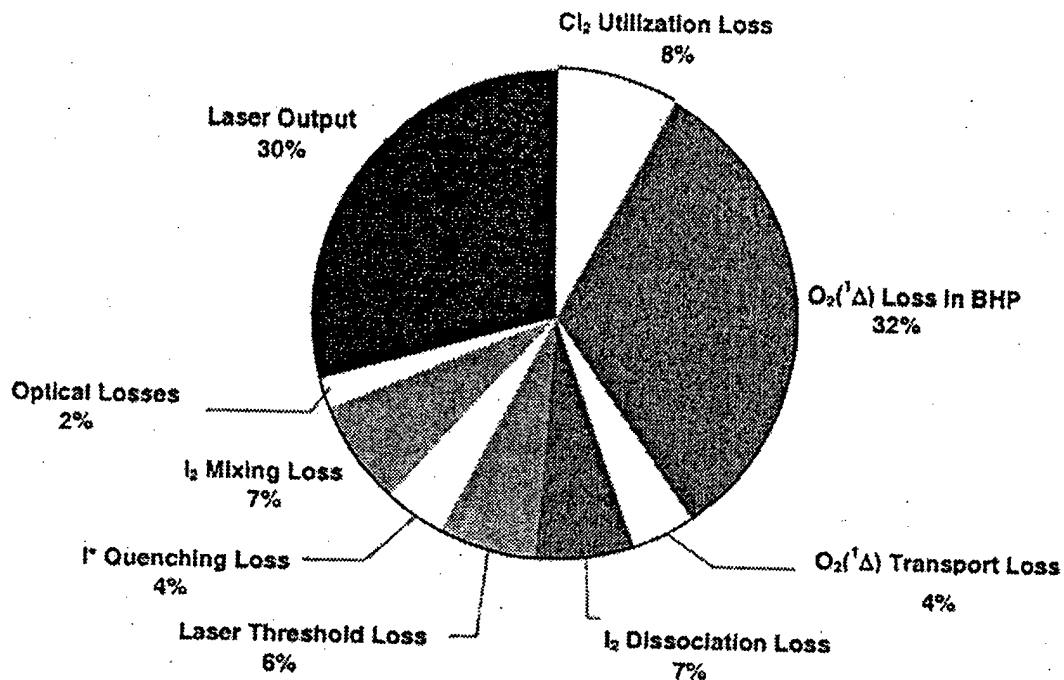


Figure 7. Allocation of Energy Losses in Jet SOG using BHP (Vetovec et al., 2000)

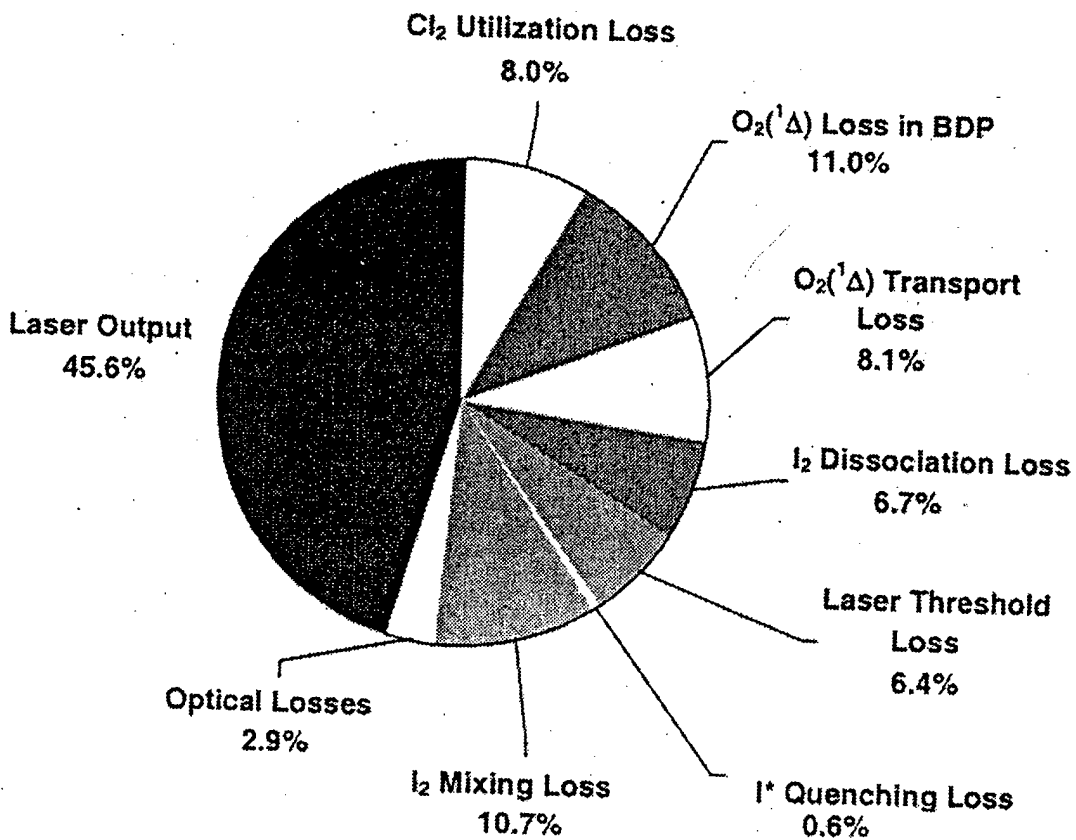


Figure 8. Allocation of Energy Losses in Jet SOG using BDP (Vetovec et al., 2000)

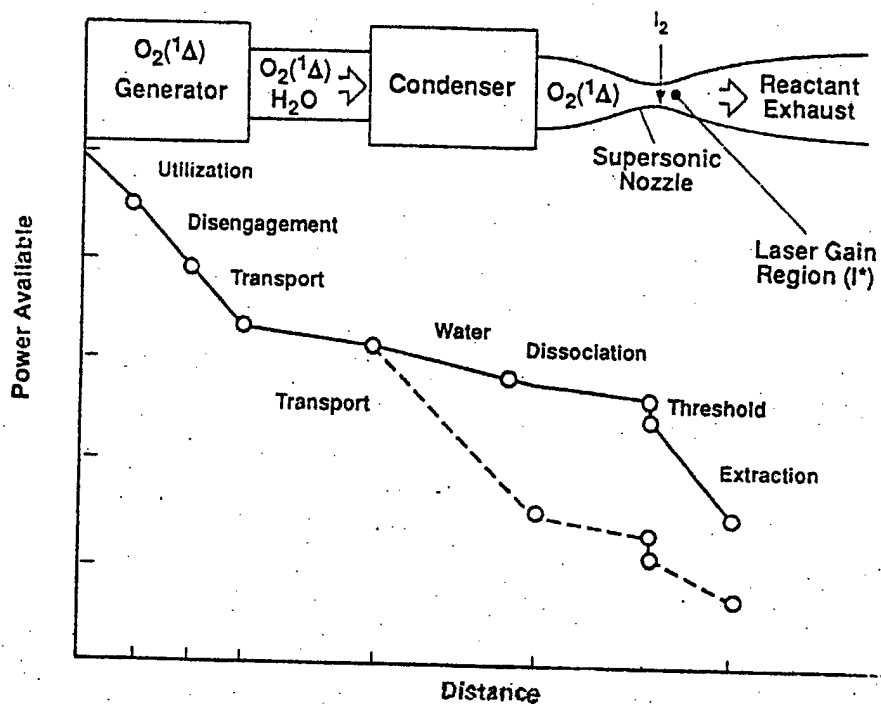


Figure 9. Power Available in the RotoCOIL System (Truesdell and Lamberson, 1992)

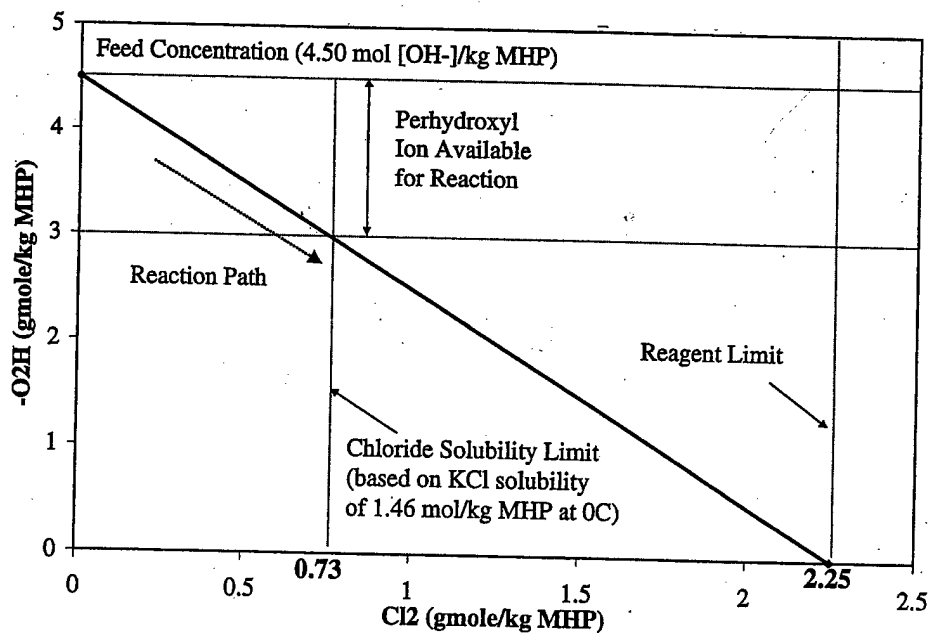


Figure 10. SOG Operating Line involving the Chlorine-BHP Reaction (Hurley and Welch, 2001)

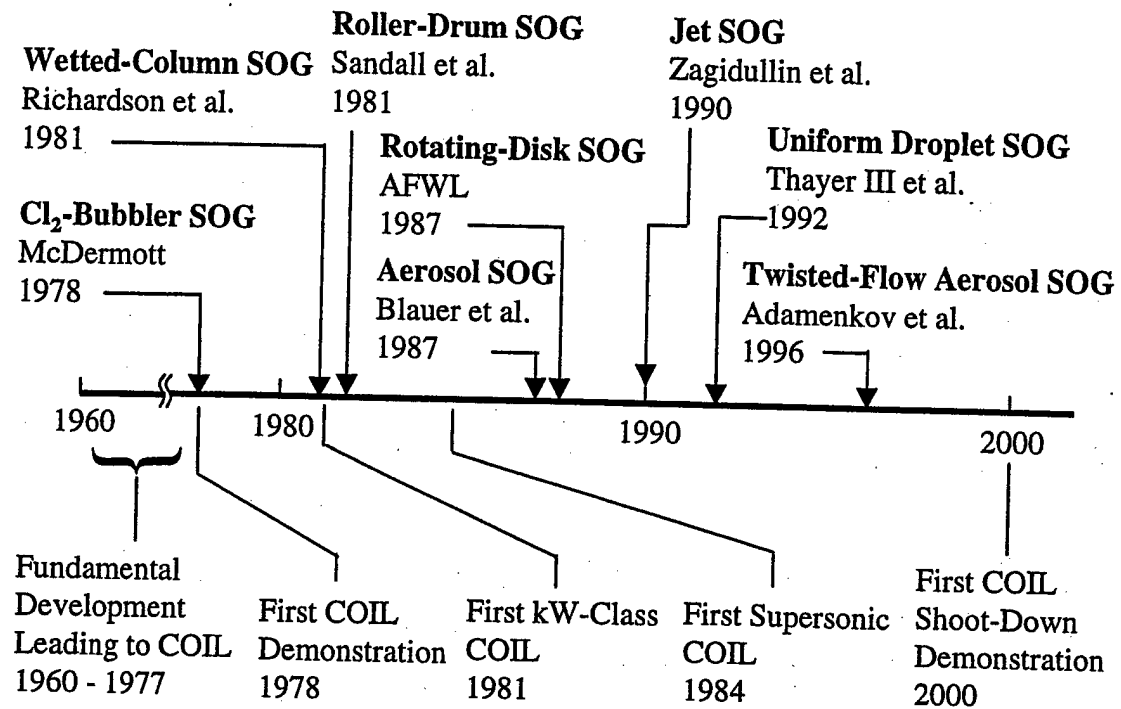


Figure 11. Milestones in the Development of SOG for COIL Applications

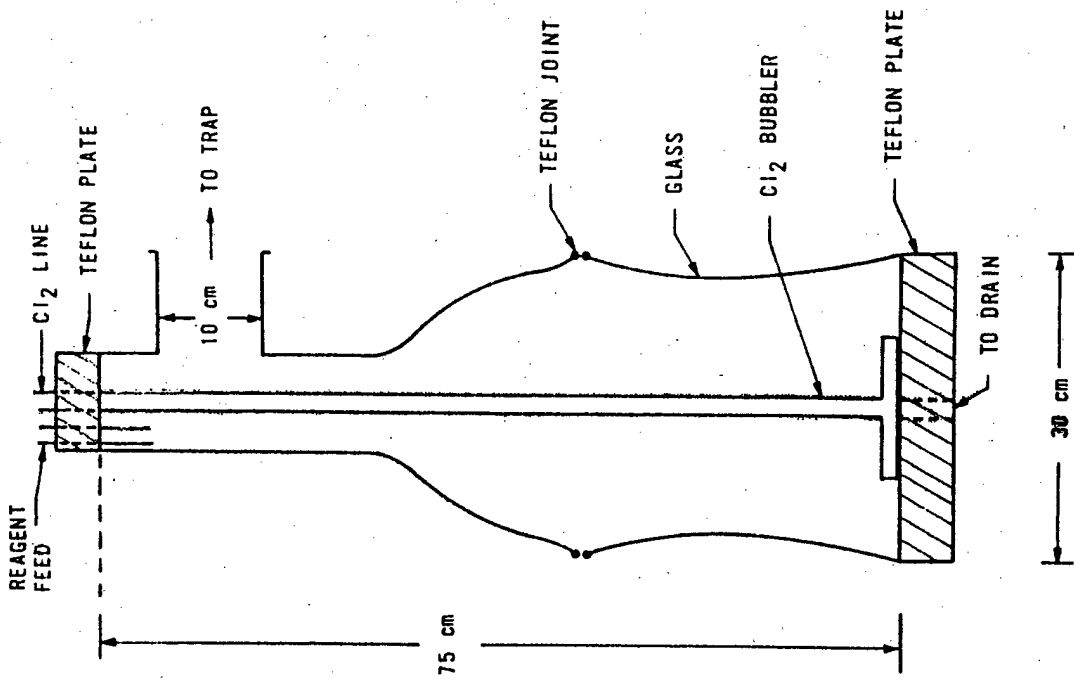


Figure 13. Chlorine Sparger SOG (Benard et al., 1979)

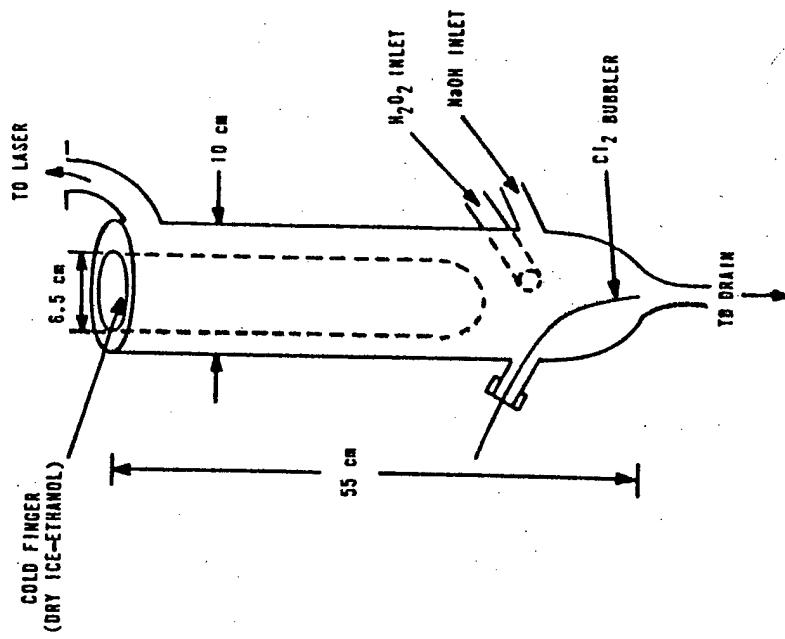


Figure 12. Chlorine Bubbler SOG (McDermott et al., 1978)

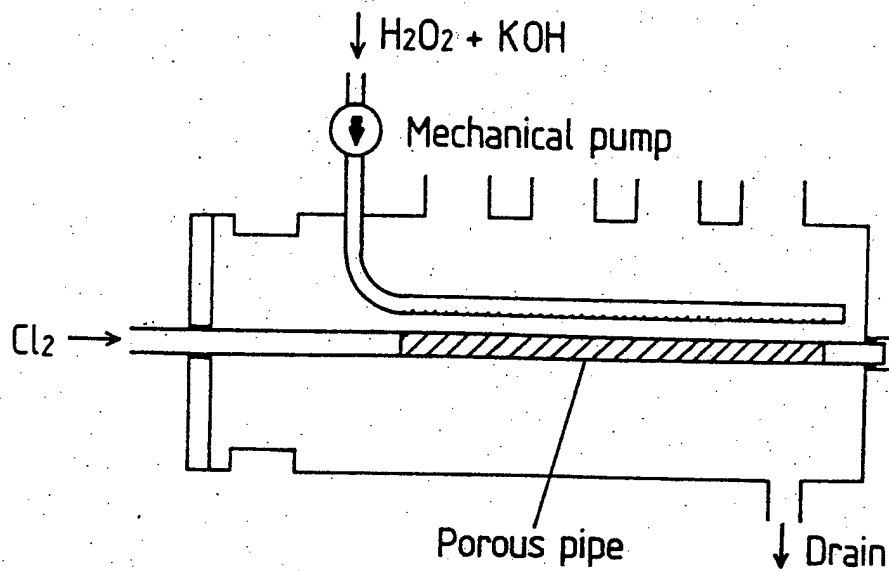


Figure 14. Fixed Porous Pipe SOG (Takejisa et al., 1987)

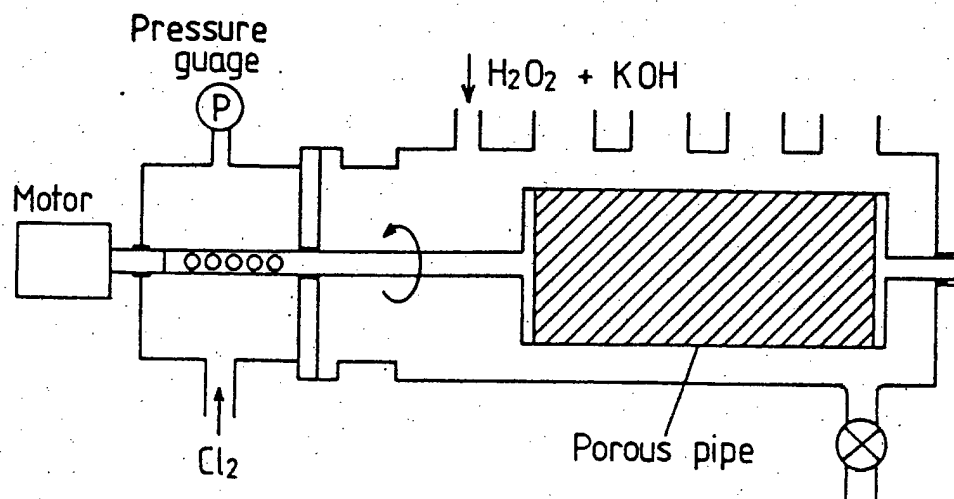


Figure 15. Rotary Porous Pipe SOG (Takejisa et al., 1987)

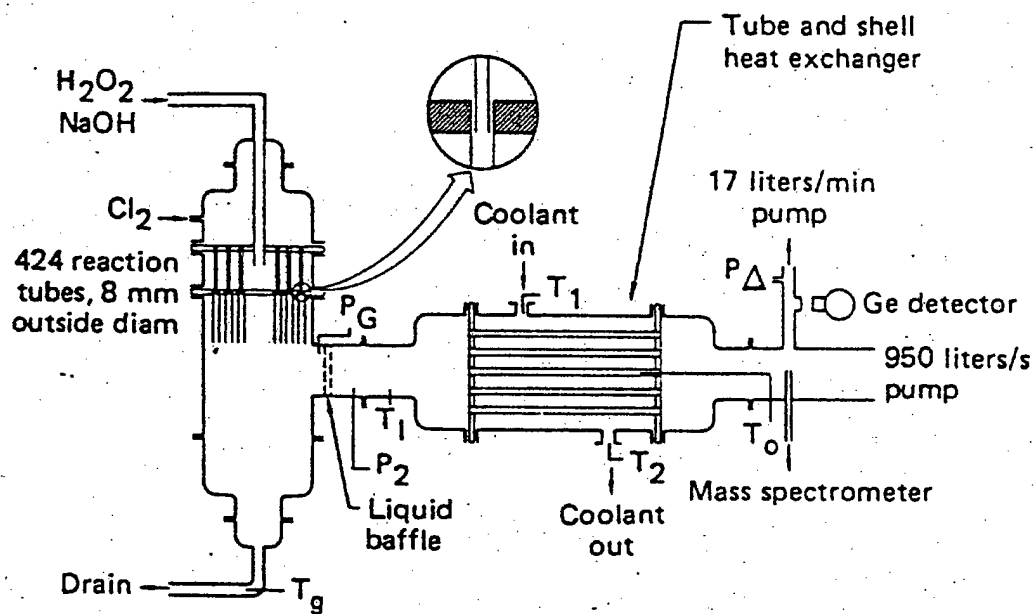


Figure 16. Wetted-Column SOG (Richardson et al., 1981)

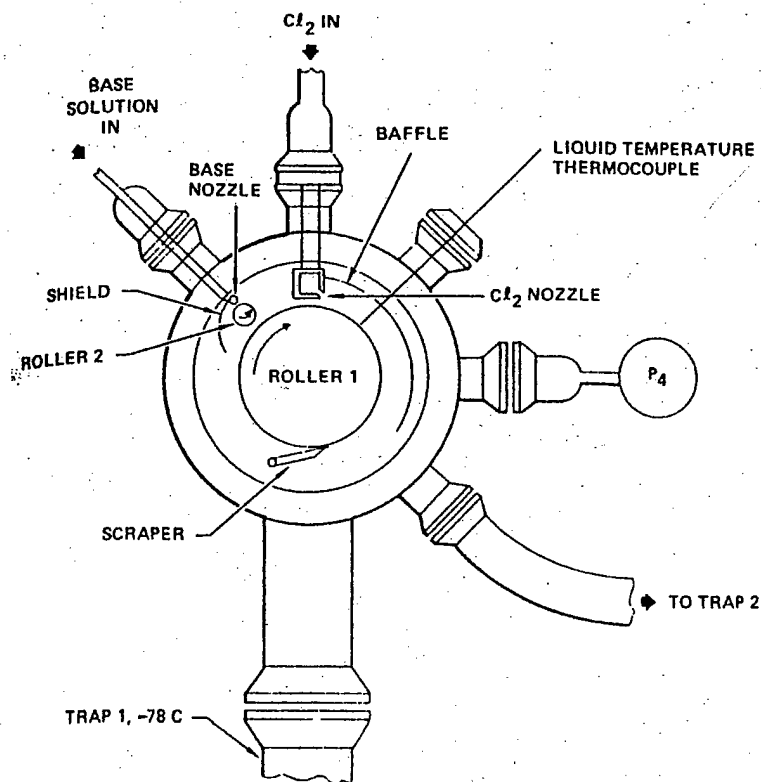


Figure 17. Roller-Drum SOG (Sandall et al., 1981)

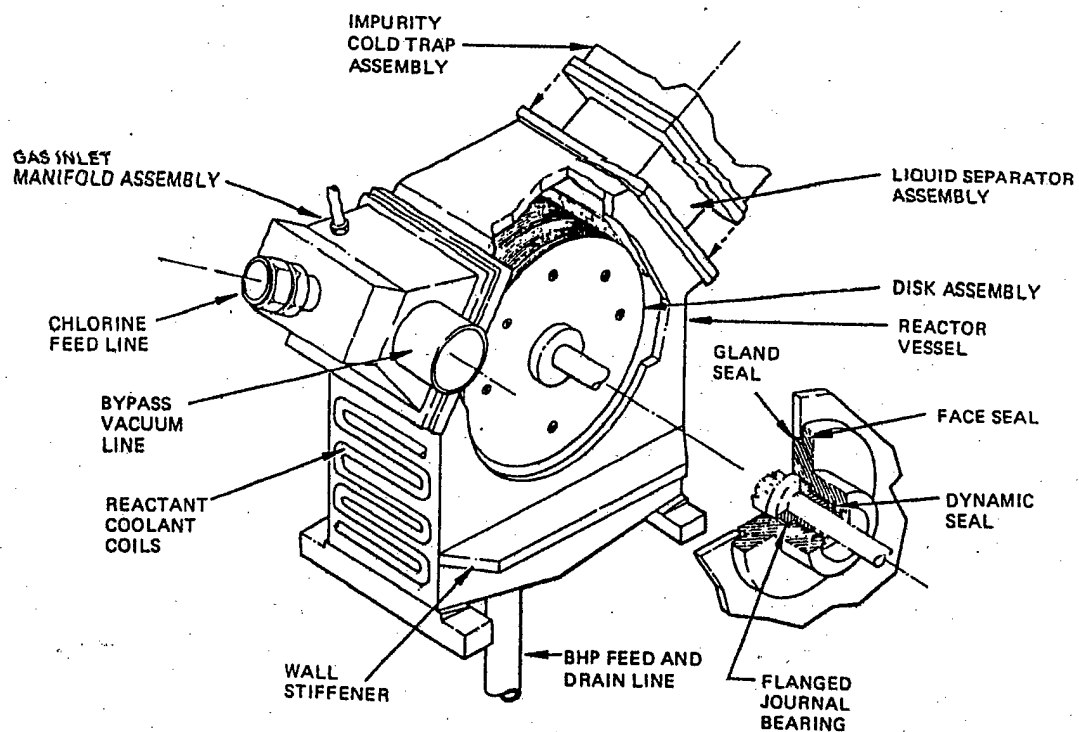


Figure 18. 3-D View of TRW Rotating Disk SOG (Harpole et al., 1992)

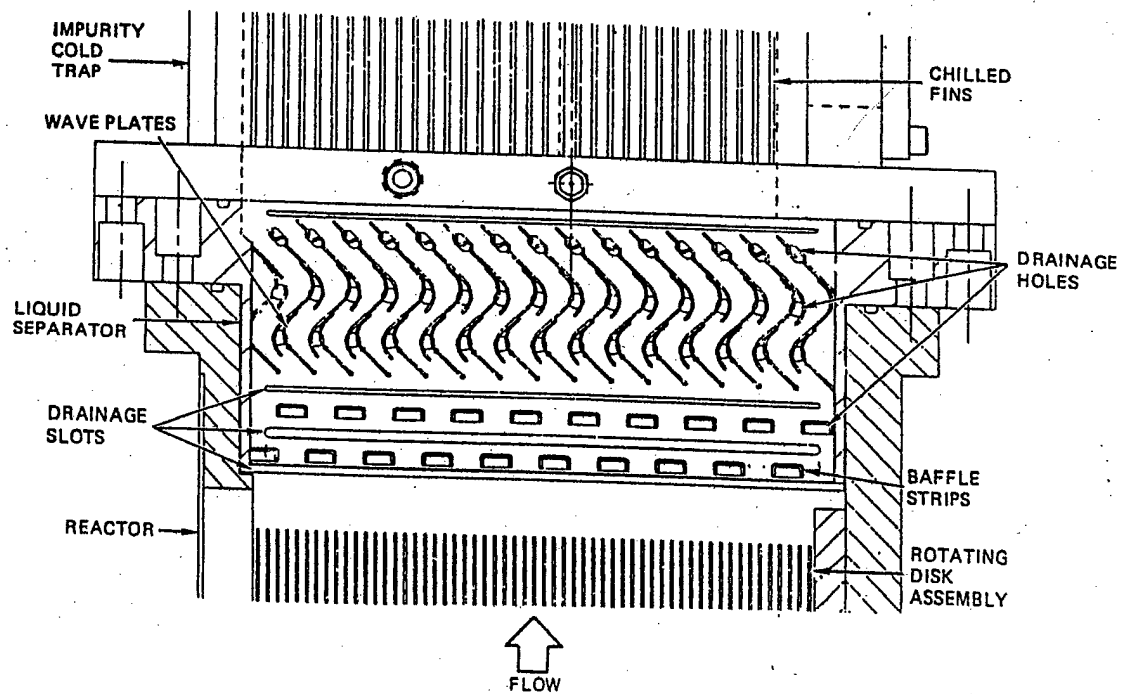


Figure 19. Liquid Separator for Rotating Disk SOG (Harpole et al., 1992)

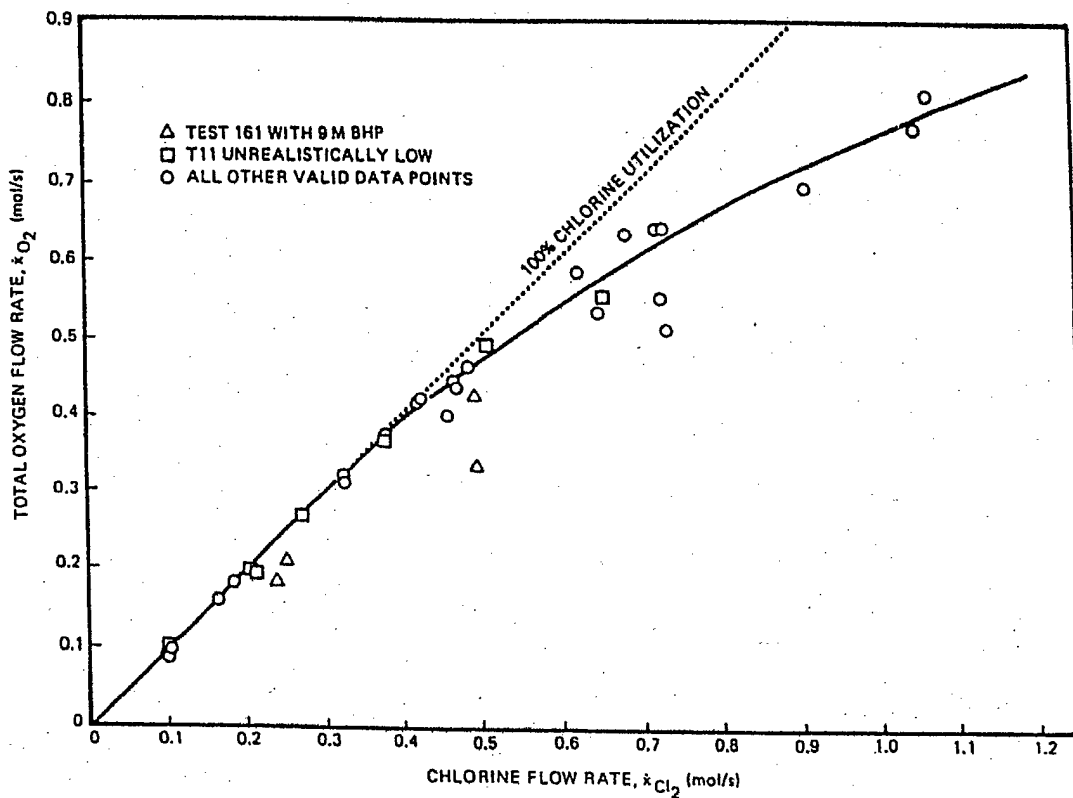


Figure 20. Dependence of the Chlorine Utilization Efficiency on Chlorine Flow Rate (Harpole et al., 1992)

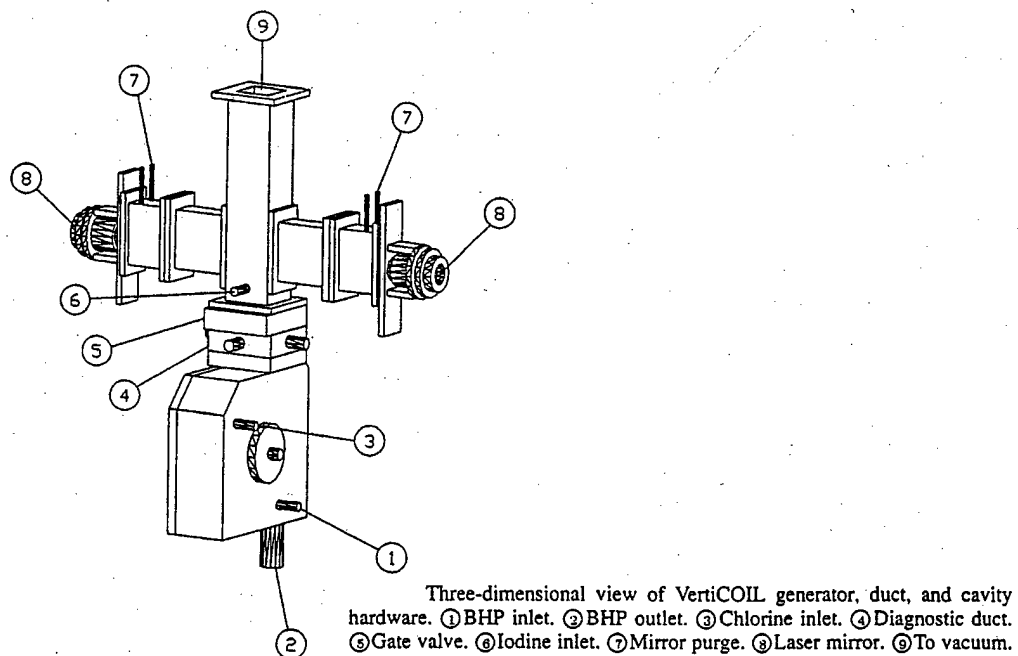


Figure 21. 3-D View of VertiCOIL Generator, Duct, and Cavity Hardware (Tilghman et al., 1999)

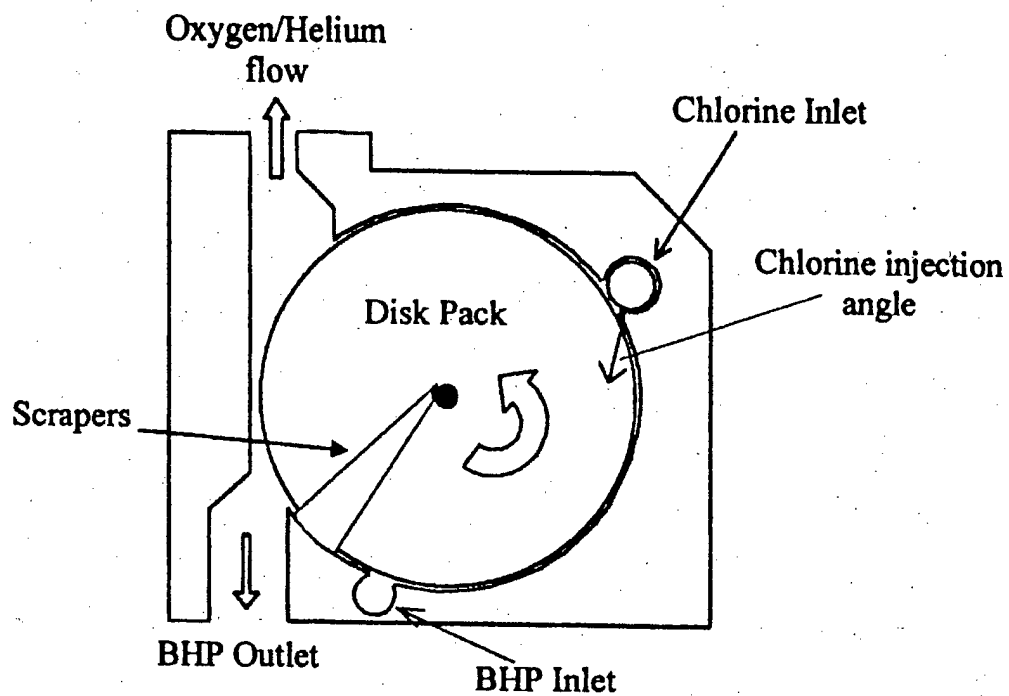


Figure 22. Schematic Illustration of VertiCOIL Rotating-Disk SOG Components (Tilghman et al., 1999)

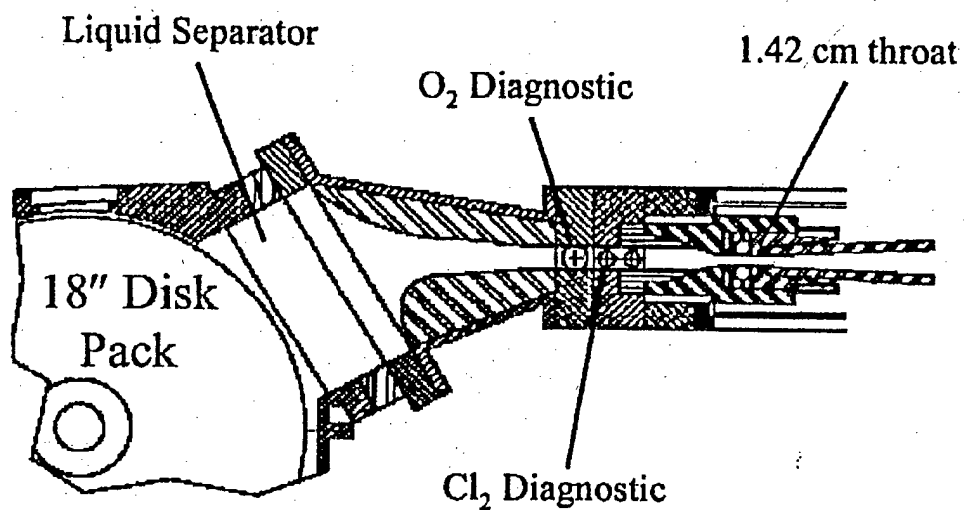


Figure 23. Cut-Away Diagram of RADICL Rotating-Disk SOG (Kendrick et al., 1999)

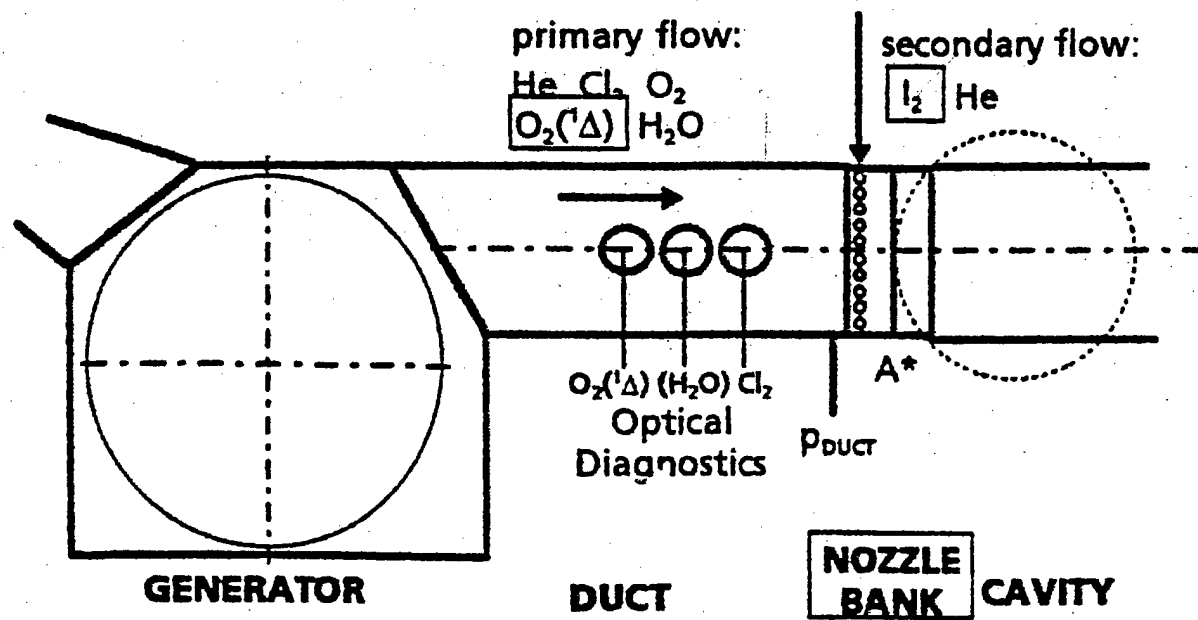
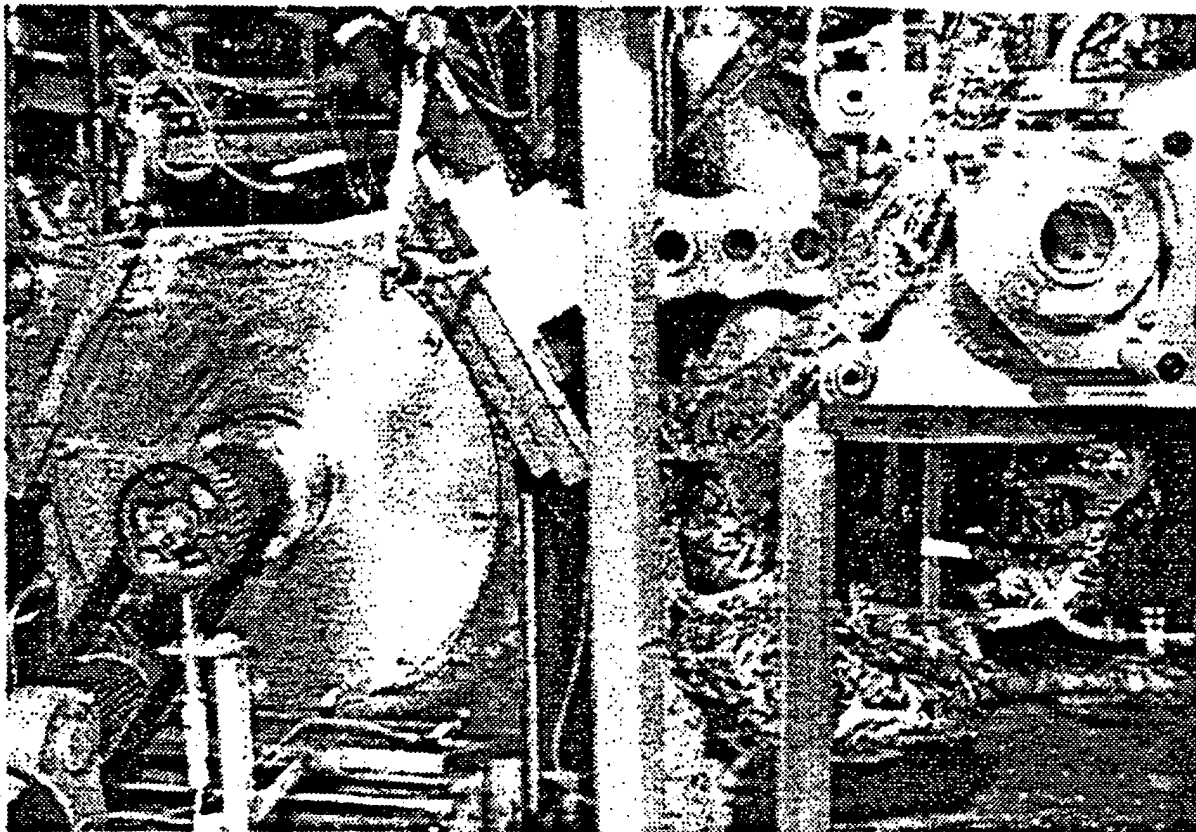
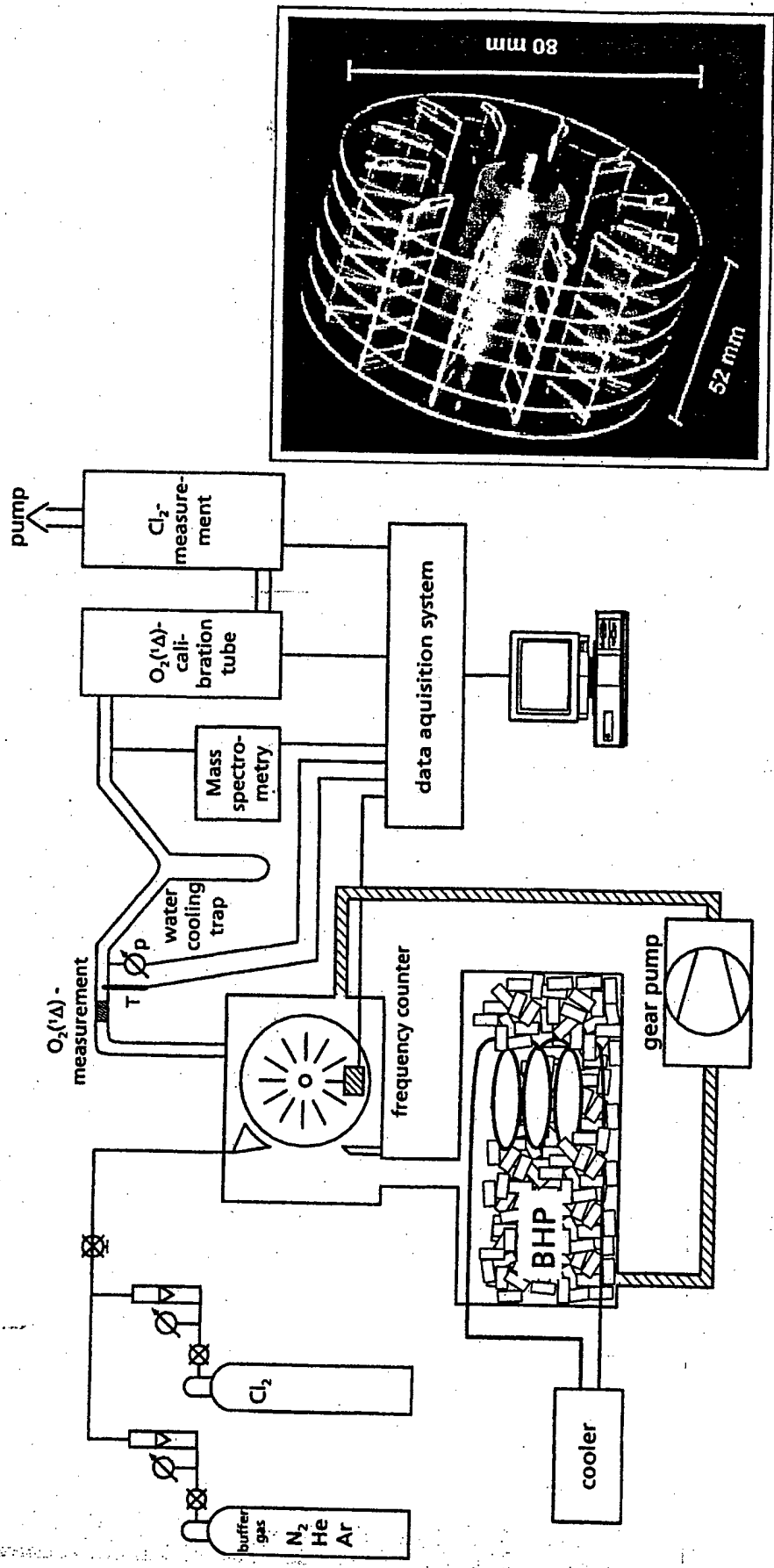
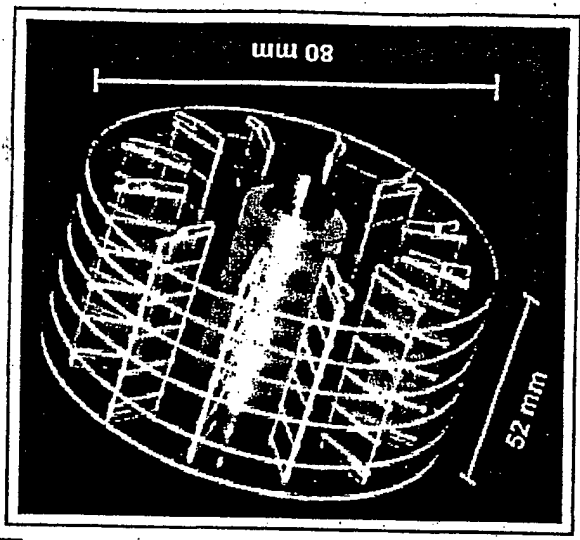


Figure 24. Photo and Sketch of COIL Setup at DRL (Grunewald et al., 1998)



(1) Schematic diagram of the Autodisk singlet oxygen generator, the closed BHP circuit, gas supply and installed diagnostics.



(2) Pack of six polycarbonate disks.

Figure 25. Schematic of Autodisk SOG System (Duschek et al., 1998)

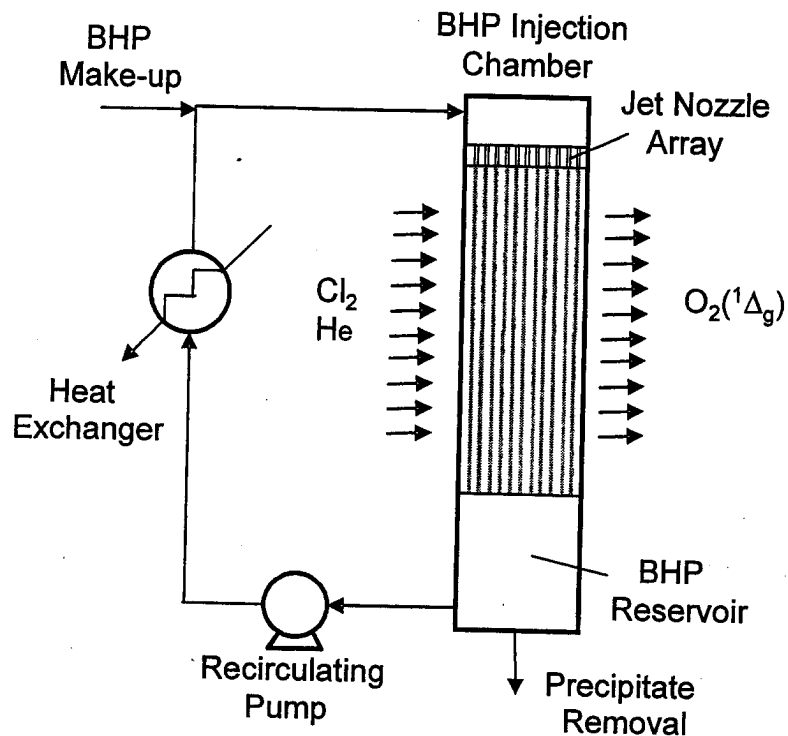
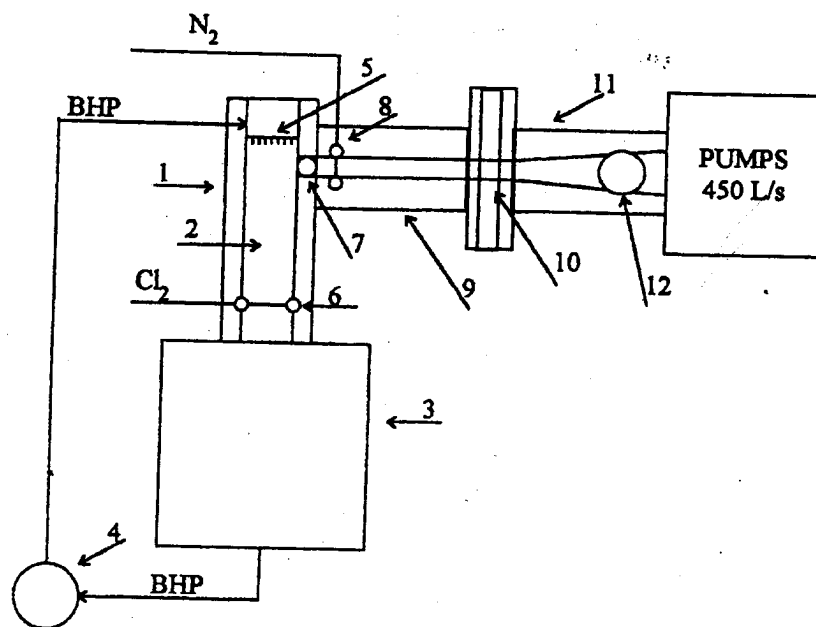


Figure 26. Schematic of a Typical Jet SOG



The experimental setup. {1} JSOG. {2} The reaction zone of BHP jets and  $\text{Cl}_2$  gas. {3} The tank for BHP. {4} Liquid gear pump. {5} Perforated plate with tubes. {6} Chlorine inlet. {7} Exit valve. {8} Primary gas injector. {9} Intermediate cell. {10} Iodine mixing system (supersonic grid nozzle). {11} Laser section. {12} Optical resonator.

Figure 27. Jet SOG Integrated with COIL (Blayvas et al., 1996)

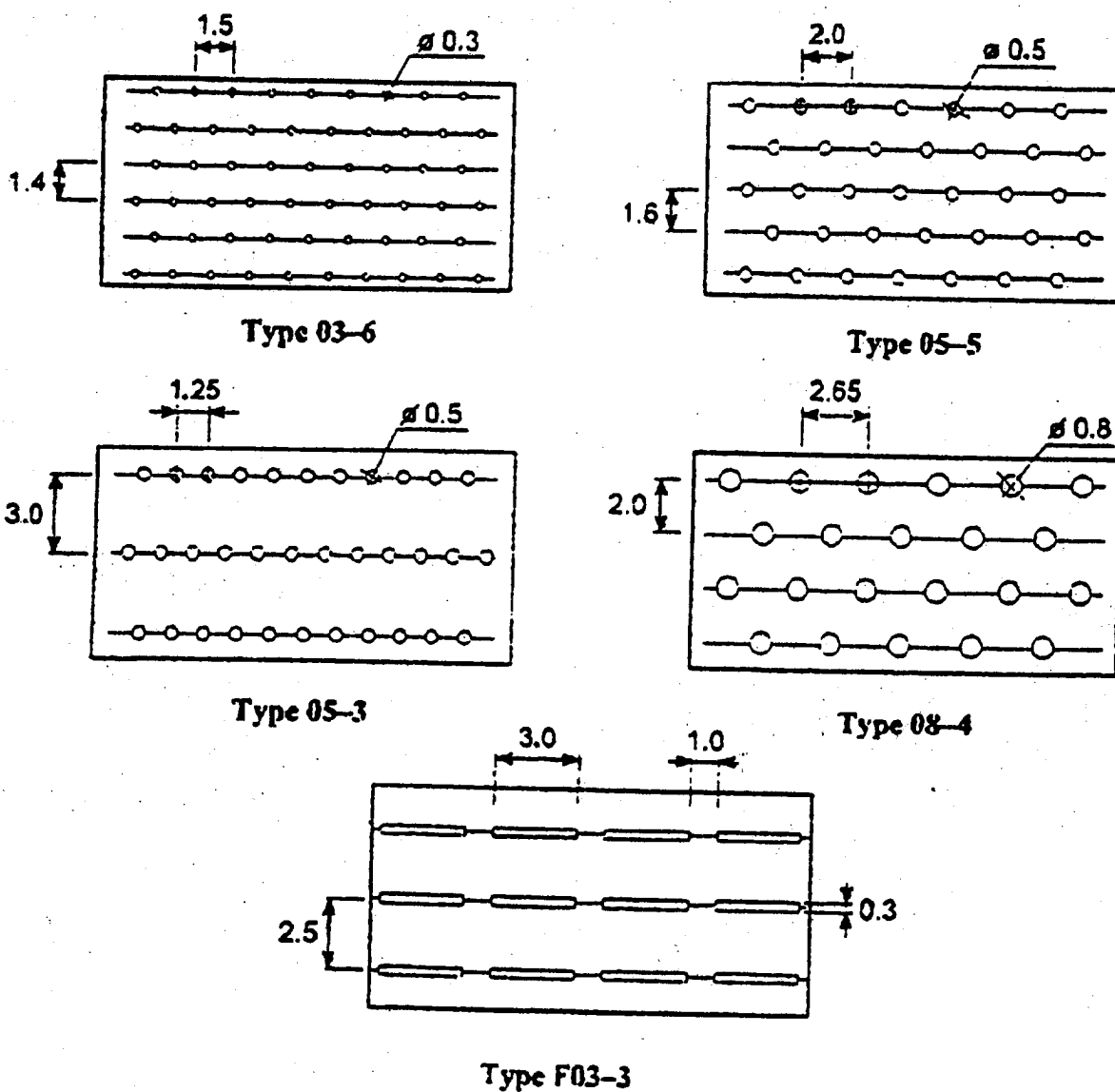


Figure 28. Jet SOG Nozzle Configurations (Kodymova et al., 1996)

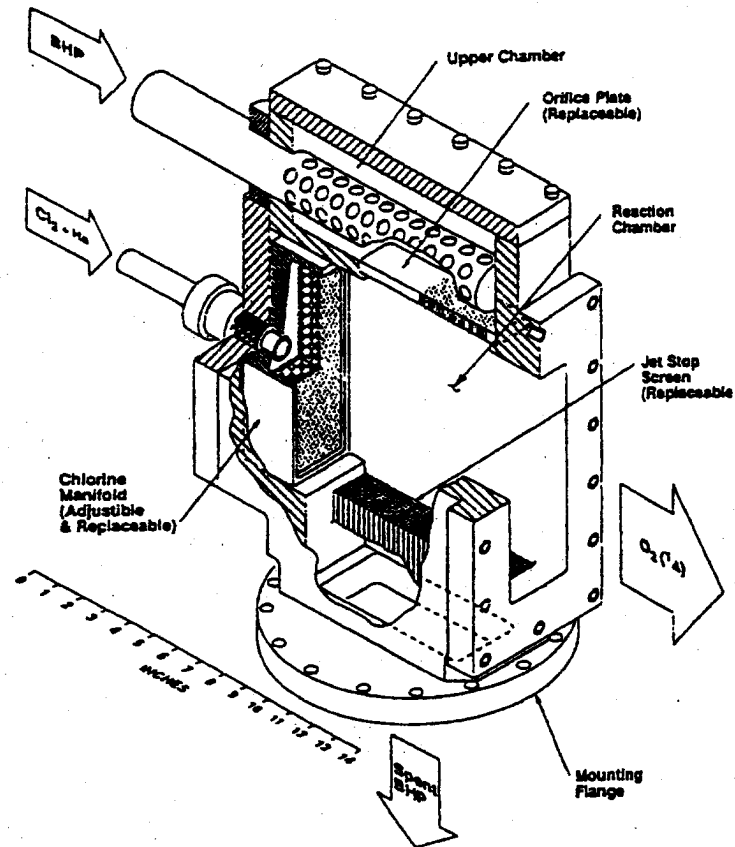


Figure 29. Rocketdyne Cross-Flow Jet SOG (McDermott et al., 1997)

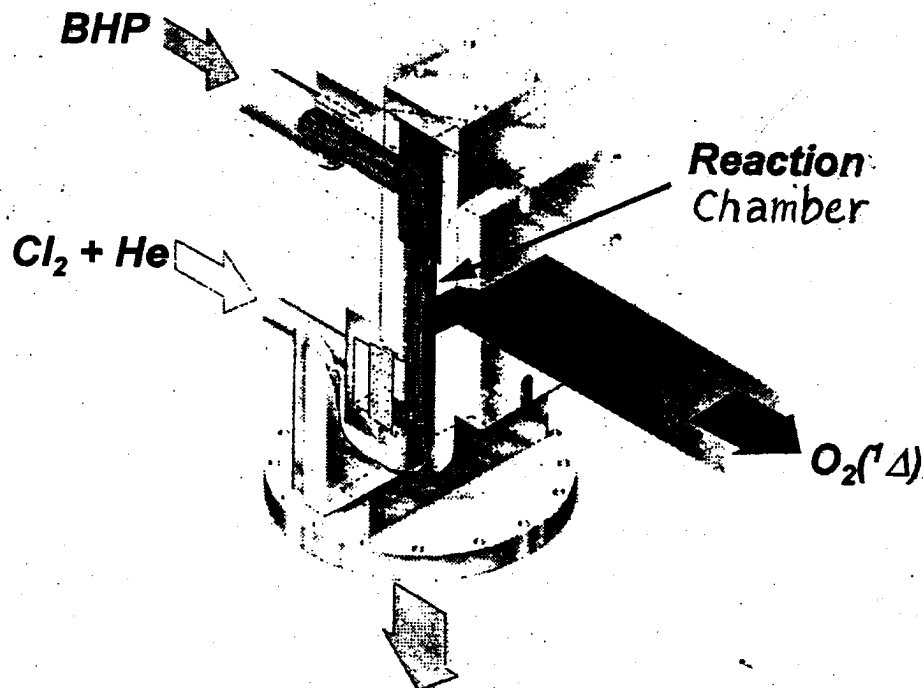
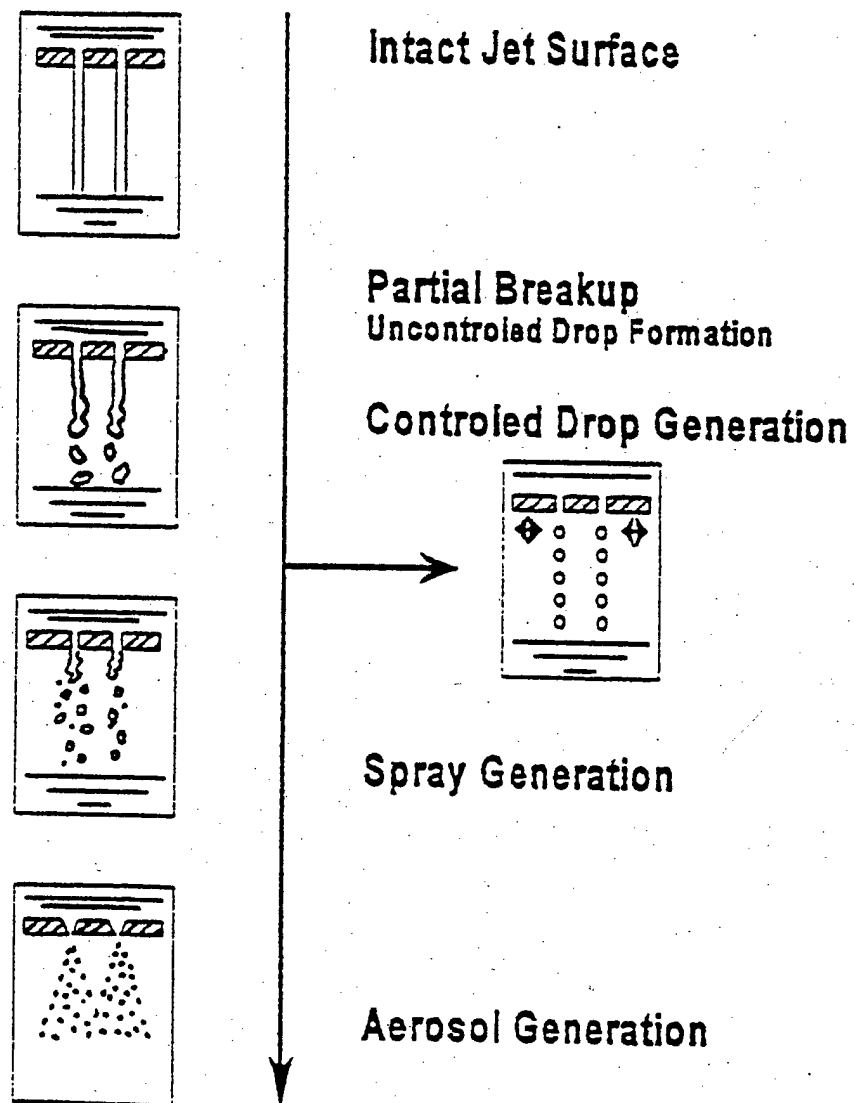


Figure 30. Rocketdyne Counter-Flow Jet SOG (McDermott et al., 1997)



**Figure 31. Progressive Transition in Flow Patterns of BHP from Ideal Jets to Aerosol**  
(Schall and Kraft, 1996)

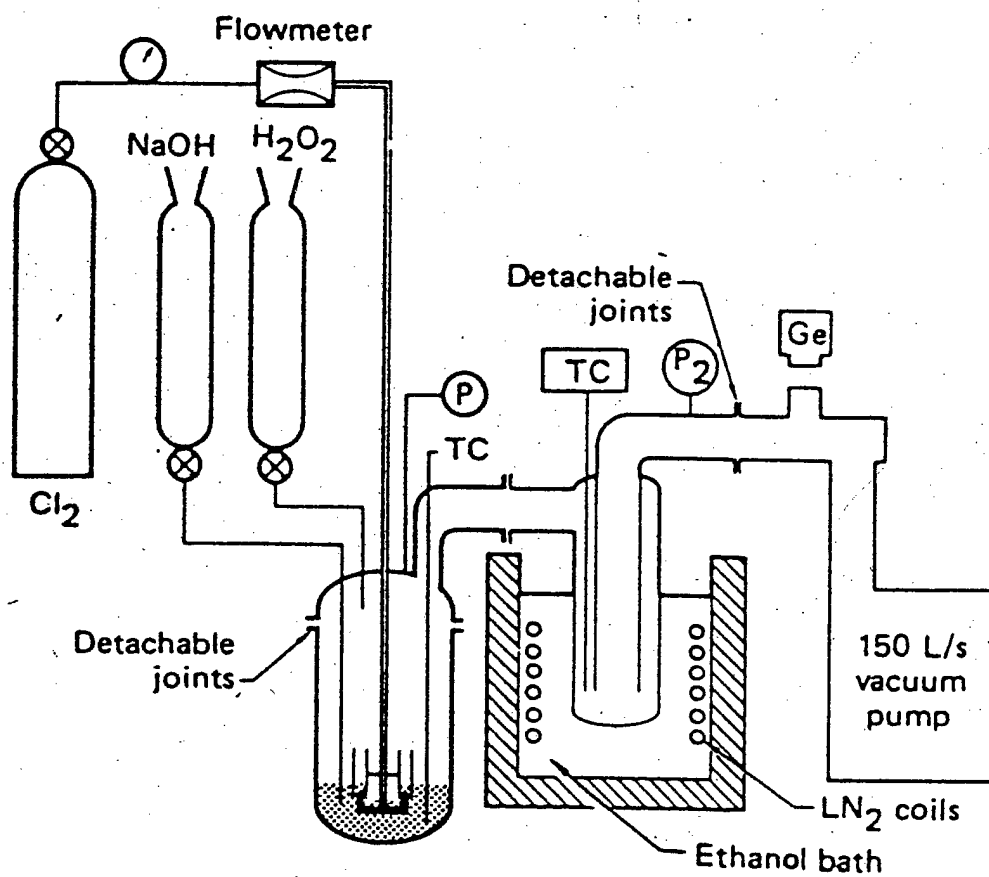


Figure 32. Schematic of Atomizer Spray SOG (Richardson et al., 1981)

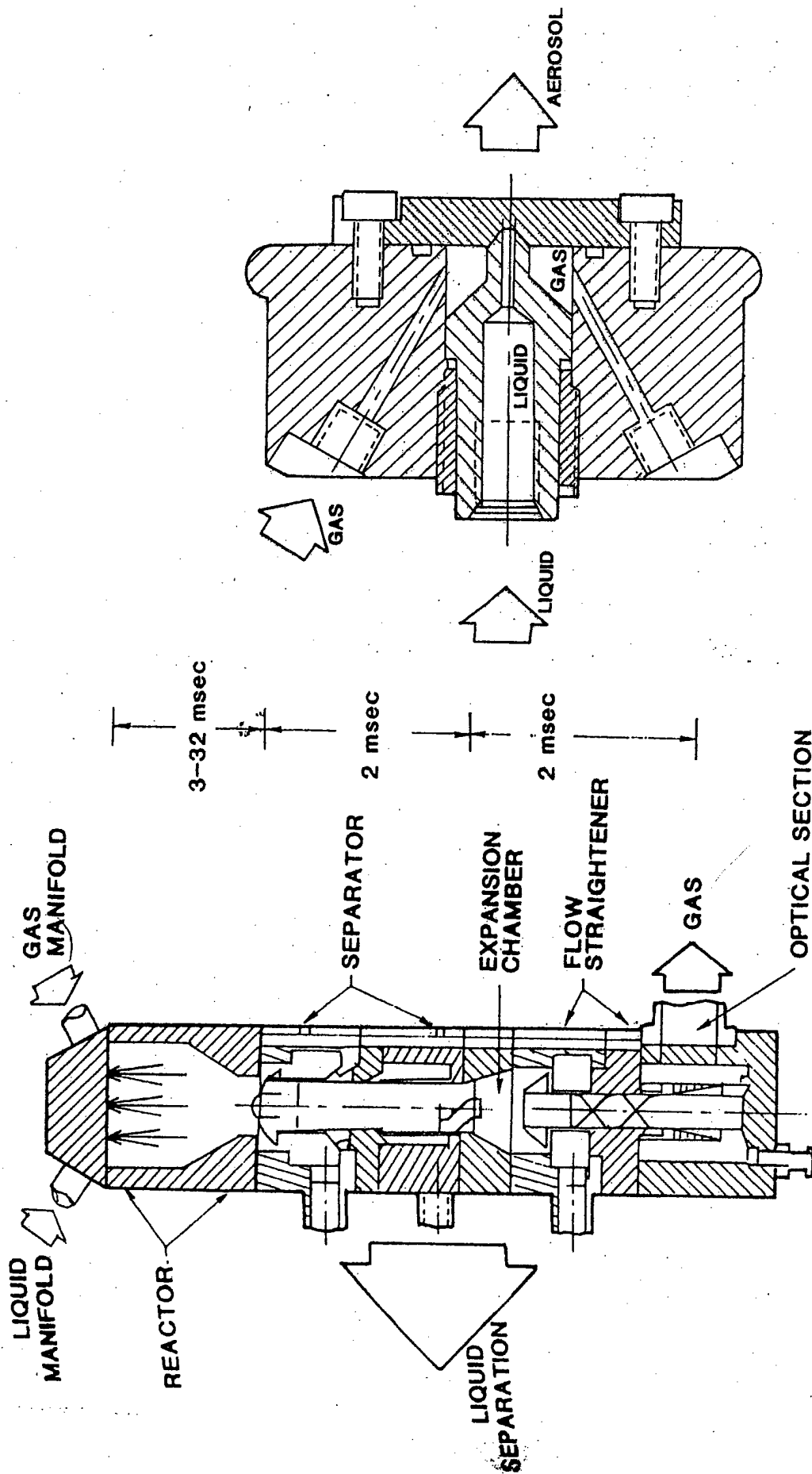


Figure 33. Schematic of Rocketdyne's Aerosol SOG (Blauer et al., 1987)

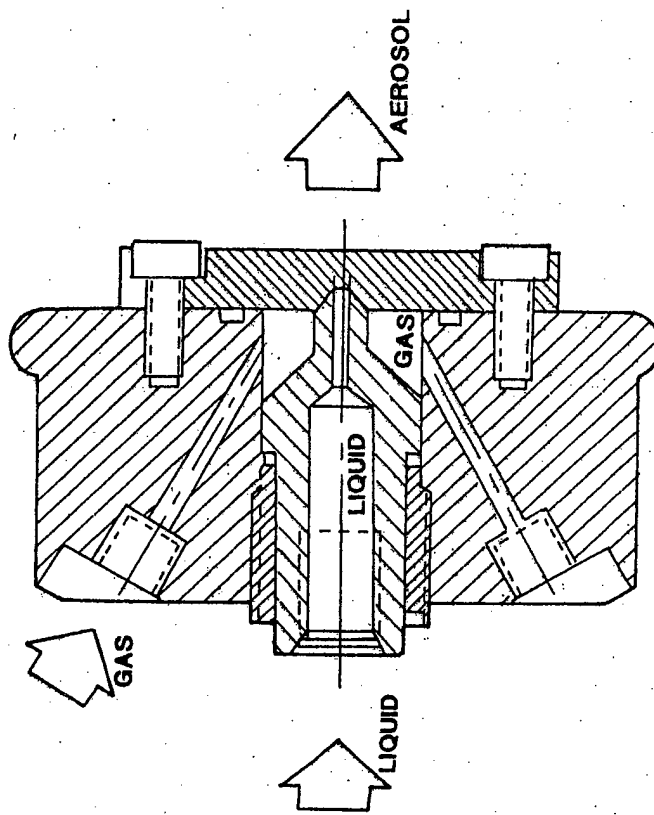


Figure 34. Schematic of Coaxial Pentad Injector Element of the Aerosol SOG (Blauer et al., 1987)

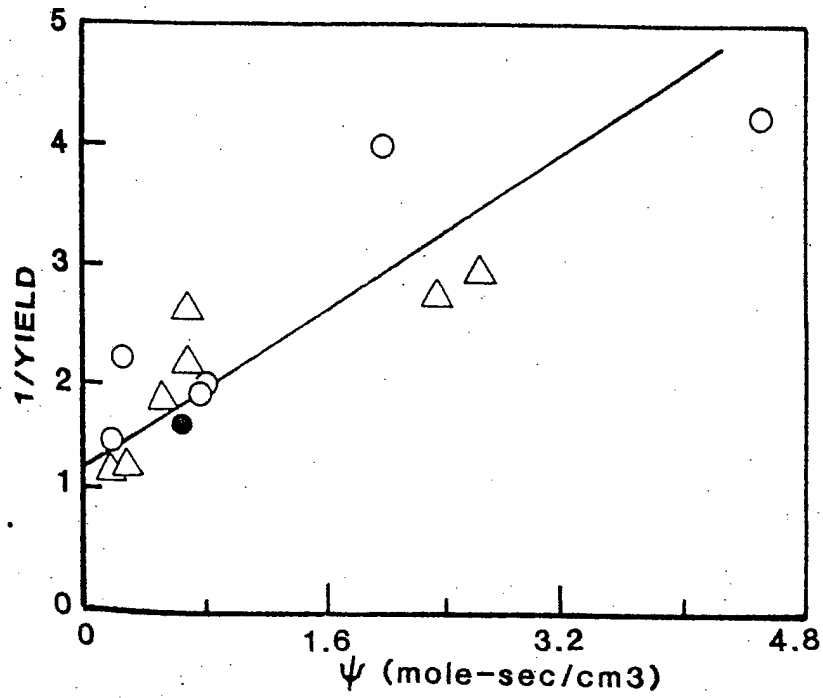


Figure 35. Correlation of Aerosol SOG Test Results (Blauer et al., 1987)

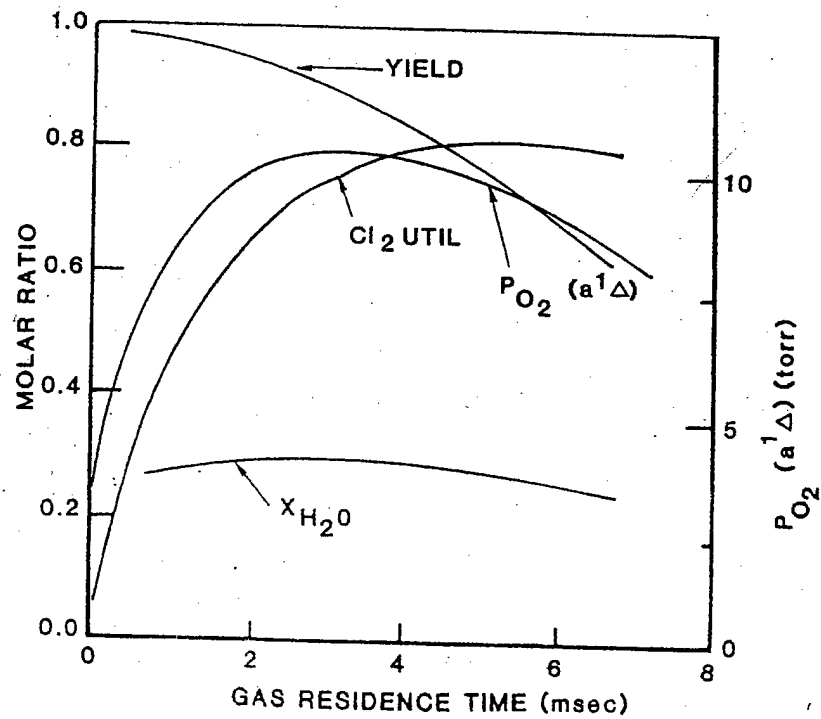


Figure 36.  $O_2(^1\Delta_g)$  Yield and Species Concentrations as a Function of Time (Blauer et al., 1987)

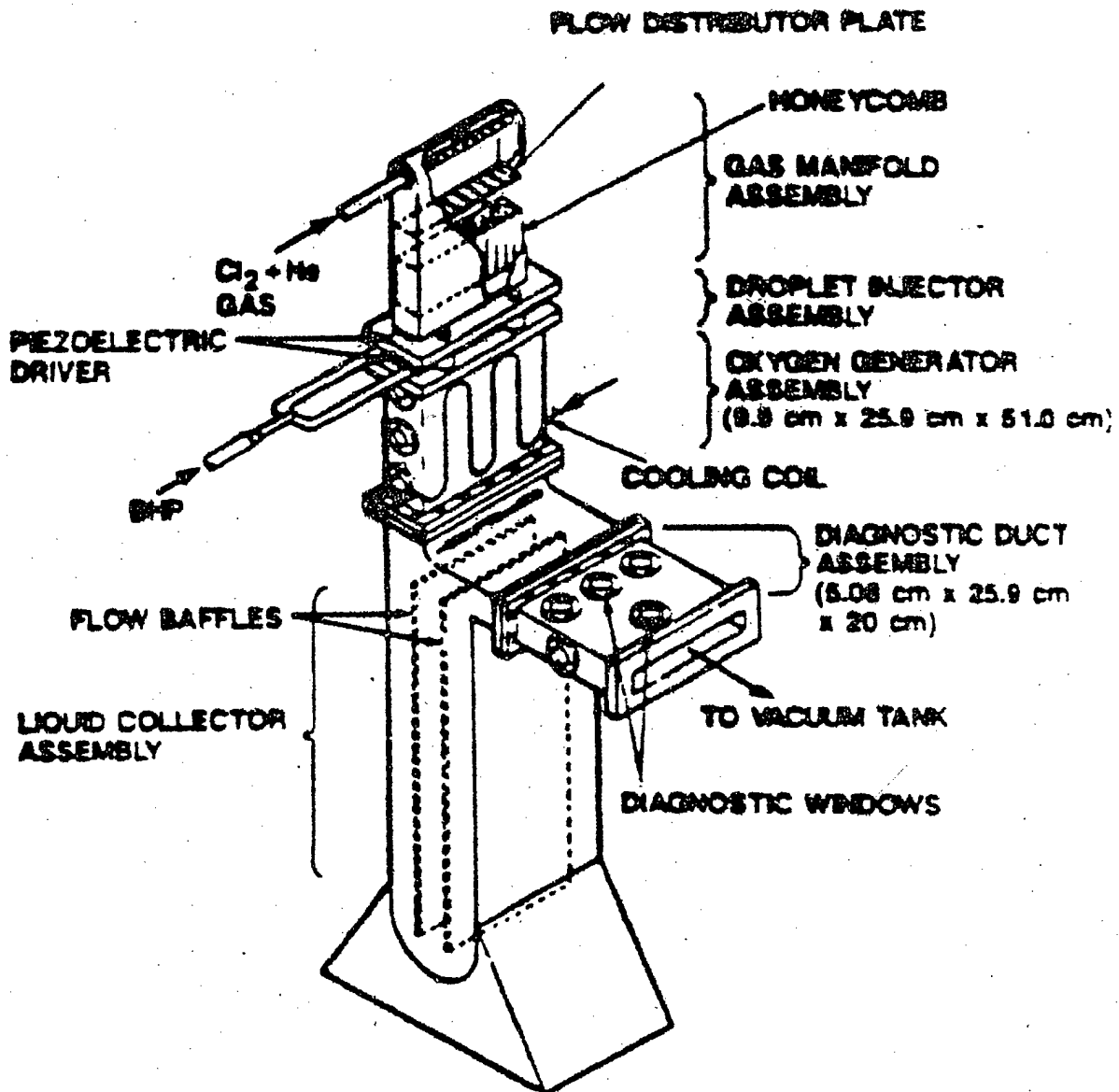


Figure 37. Schematic of Uniform Droplet SOG (Thayer III, 1992)

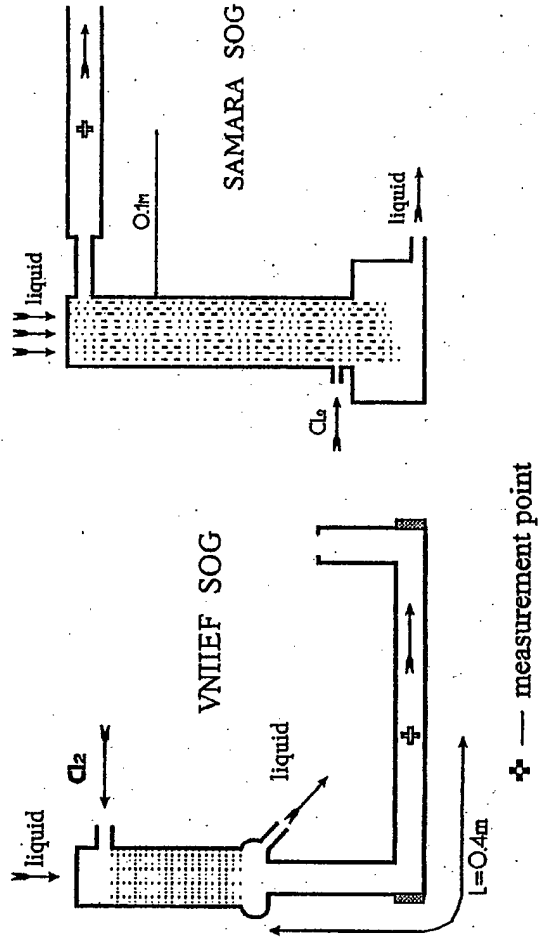
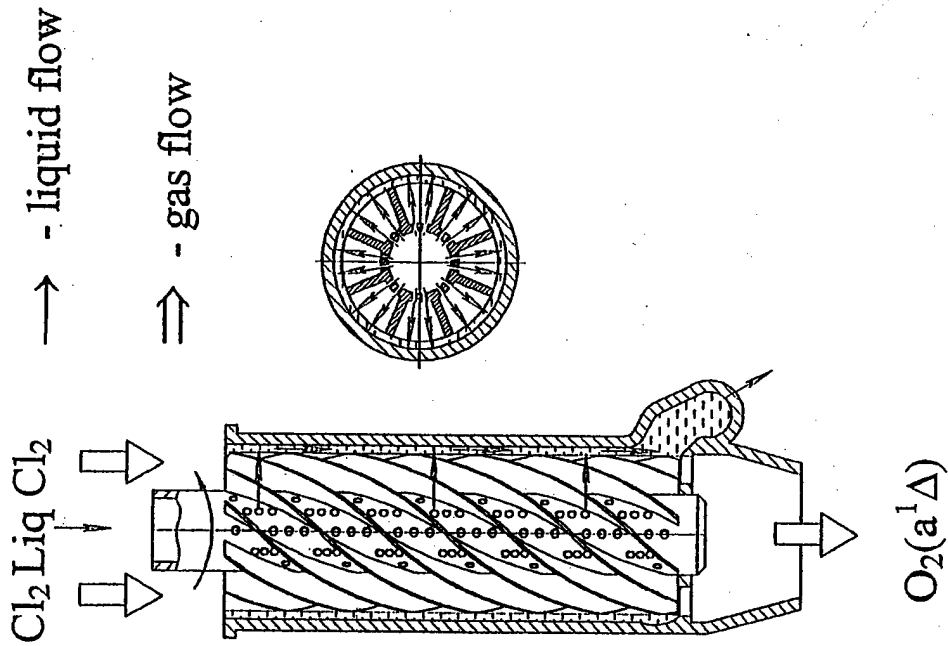


Figure 38. Schematic of Aerosol-Jet Hybrid SOG (Adamenkov et al., 1996)

Figure 39. Comparison of System Configurations for Hybrid SOG and Jet SOG (Adamenkov et al., 1996)

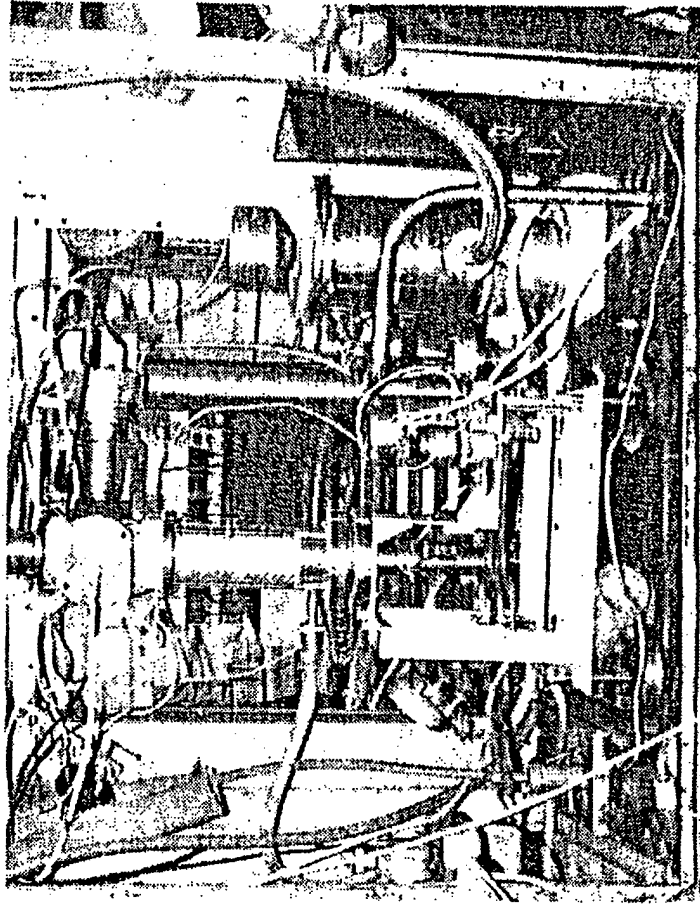


Figure 41. Photo of Twisted Aerosol SOG Test Setup  
(Krukovsky et al., 2000)

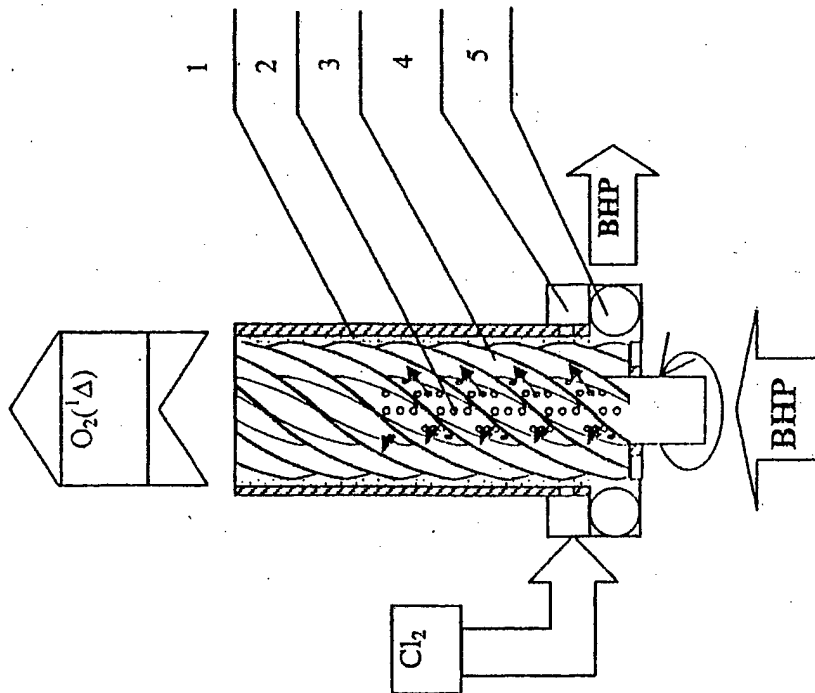


Fig. 1. Worm-type SOG layout

- 1 – cylindrical reactor body,
- 2 – holes for liquid delivery to reactor,
- 3 – 8-worm with blades,
- 4 – chlorine collector,
- 5 – spent liquid removal.

Figure 40. Schematic of Twisted Aerosol SOG  
(Krukovsky et al., 2000)

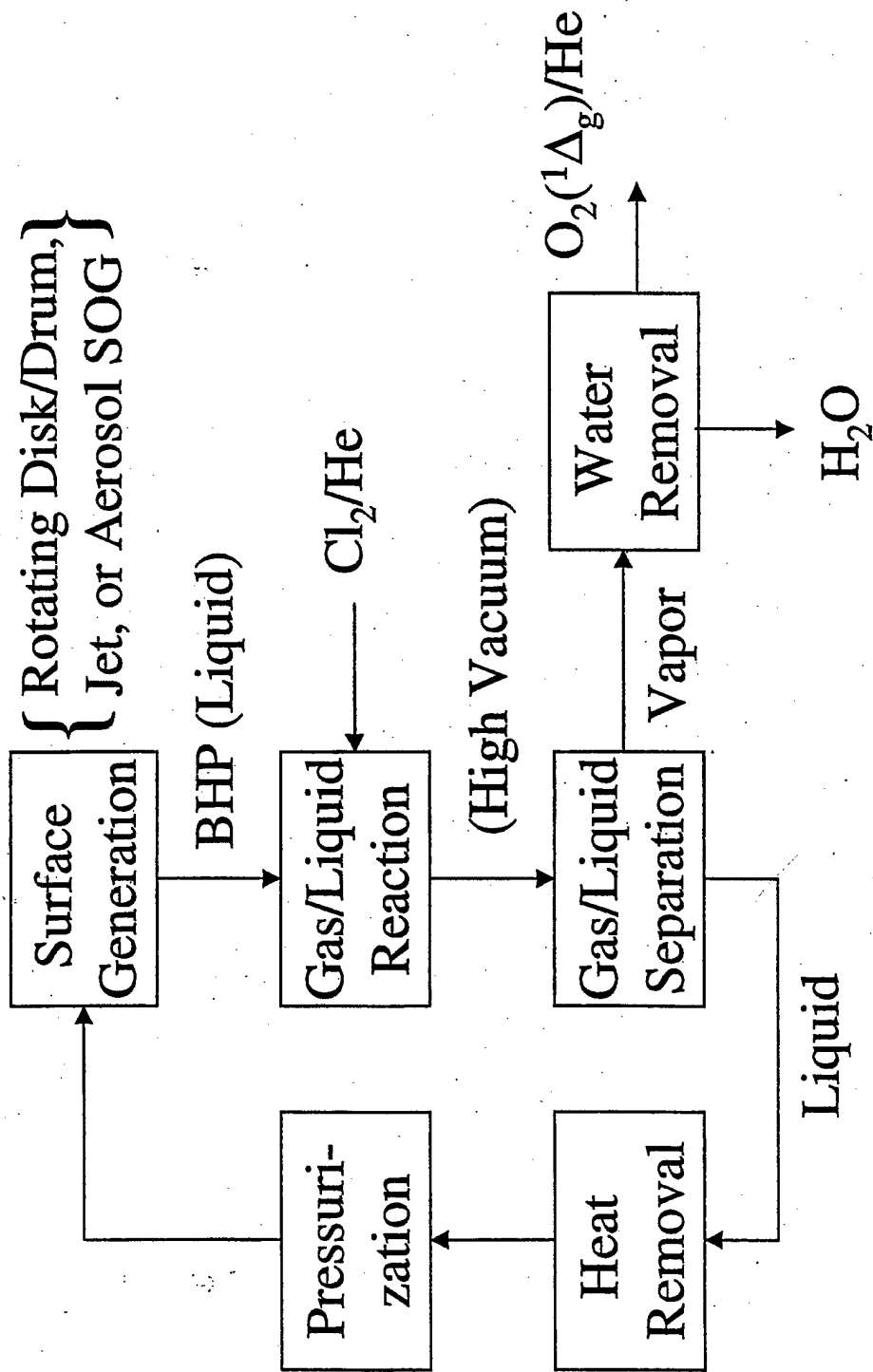


Figure 42. Design Approach Common to Existing SOGs

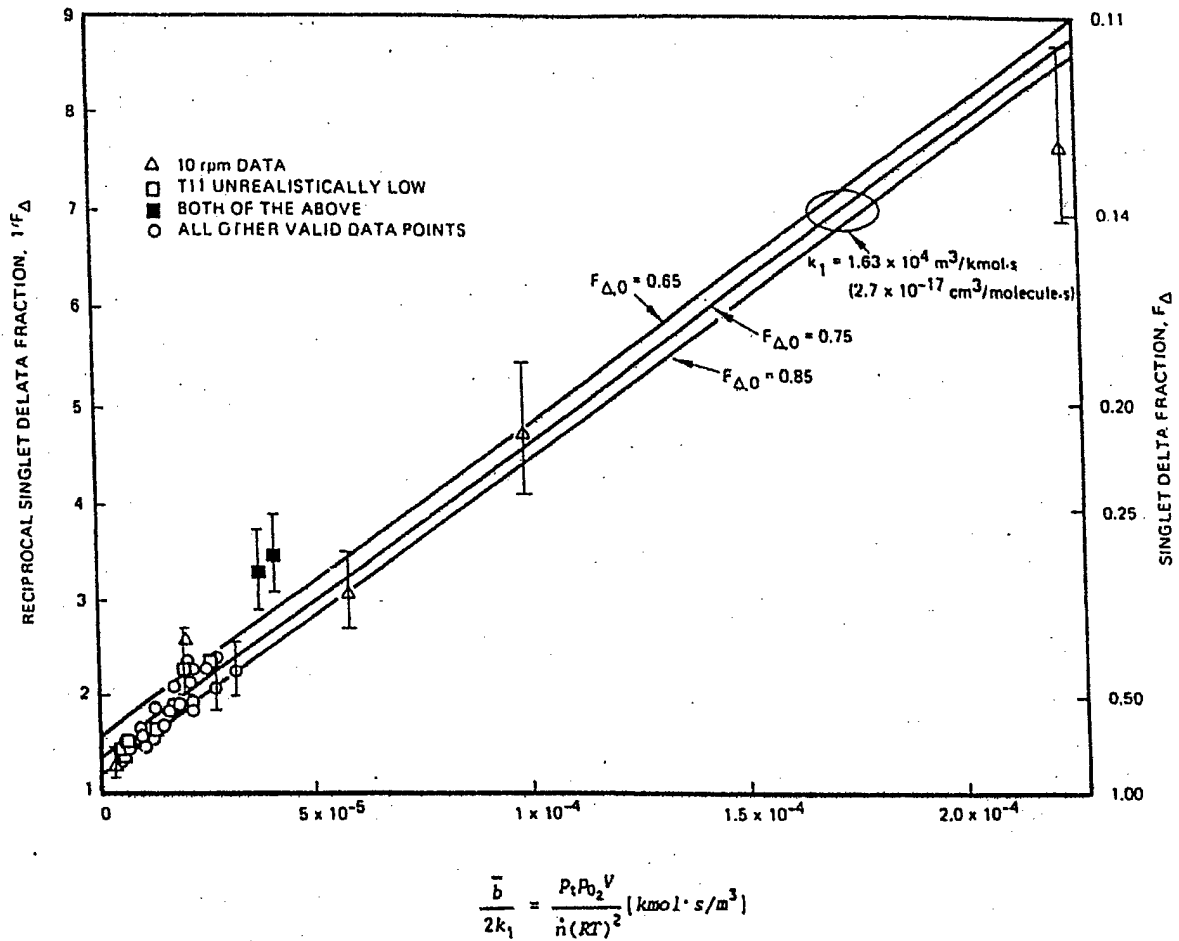


Figure 43. Experimental Data on  $O_2(^1\Delta_g)$  Fraction (Harpole et al., 1992)

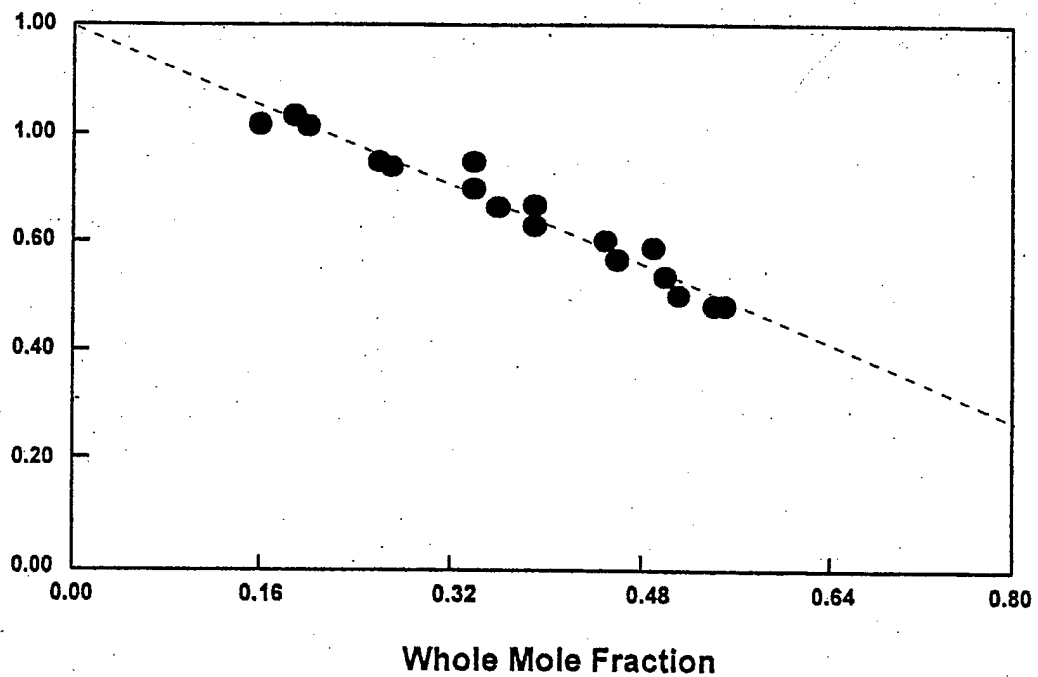


Figure 44. Effect of Water on COIL Power Output (Truesdell et al., 1995)

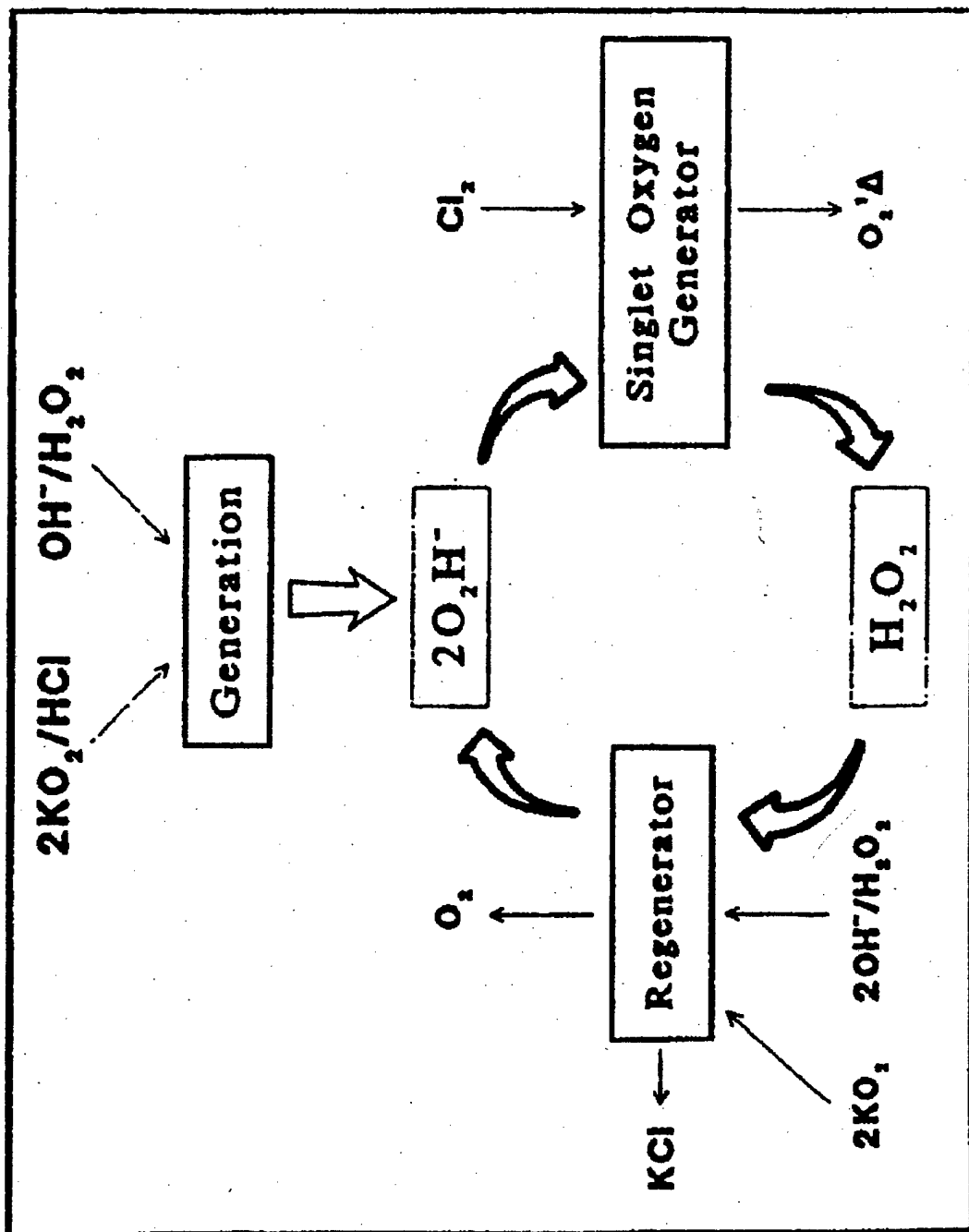


Figure 45. Proposed COIL BHP Cycle (Dinges et al., 1994)

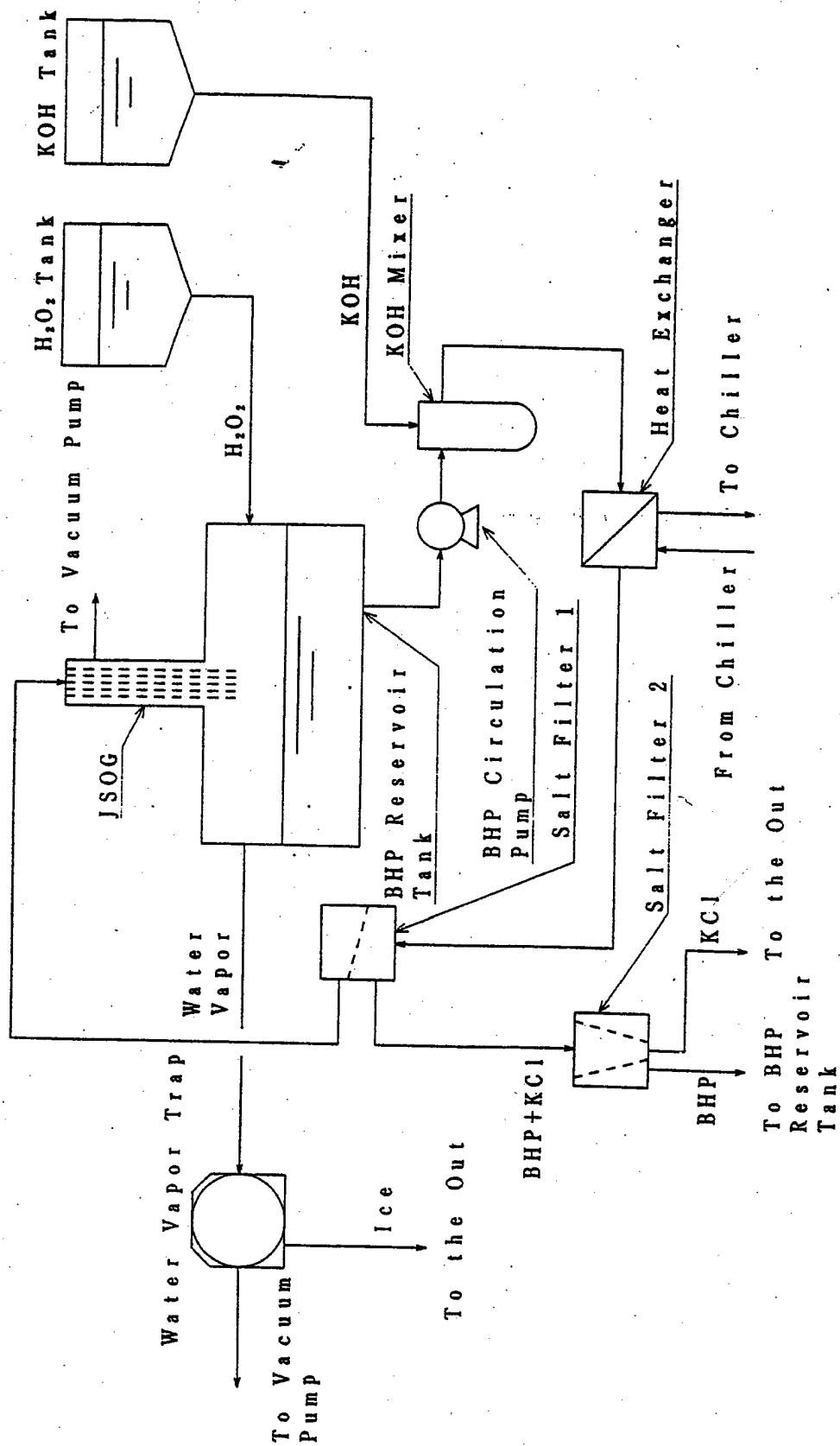


Figure 46. SOG Operation with BHP Recycling System (Naito et al., 1997)

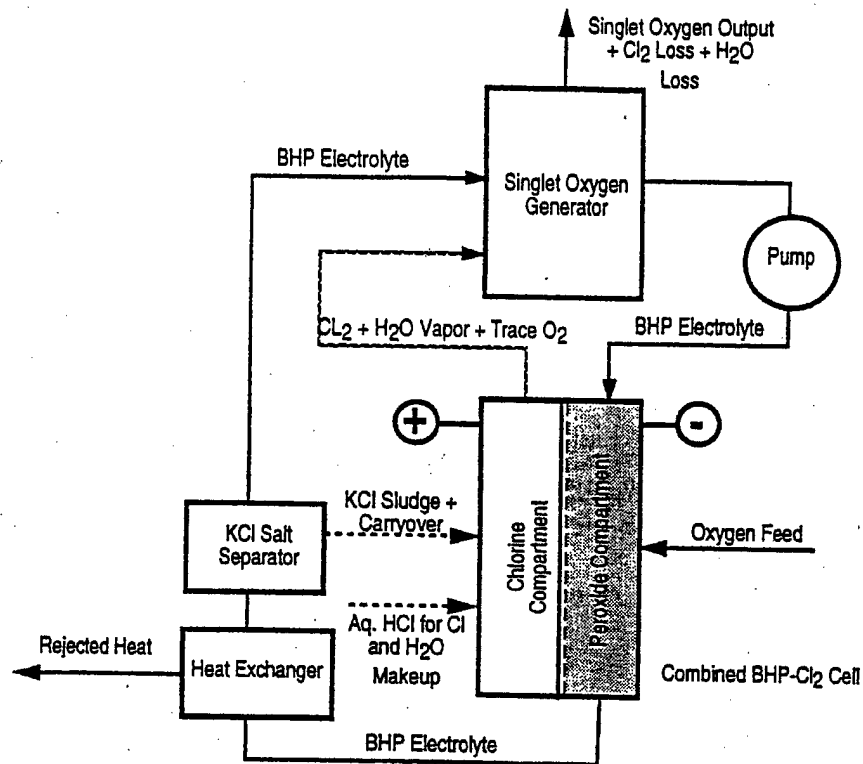


Figure 47. Schematic of Electrolytic Regeneration of BHP and Cl<sub>2</sub> (Vetrovec, 1997)

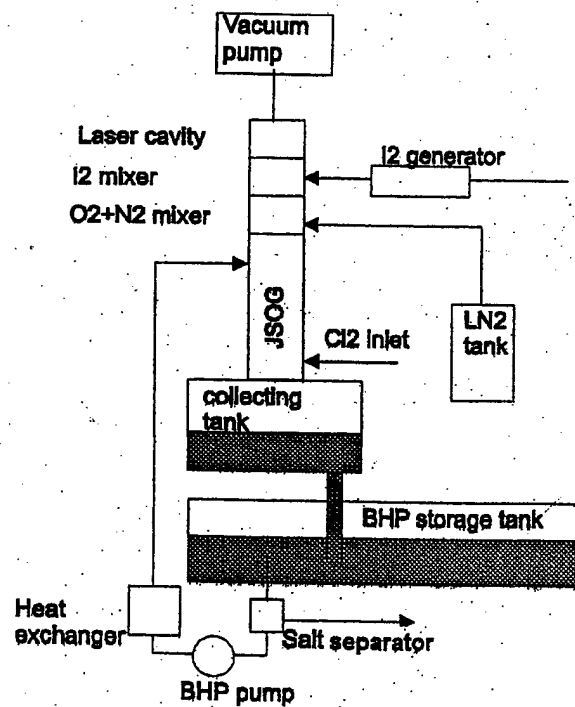


Figure 48. Simplified Process Schematic for an Industrial COIL Operation (Zagidullin and Nikolaev, 1999)

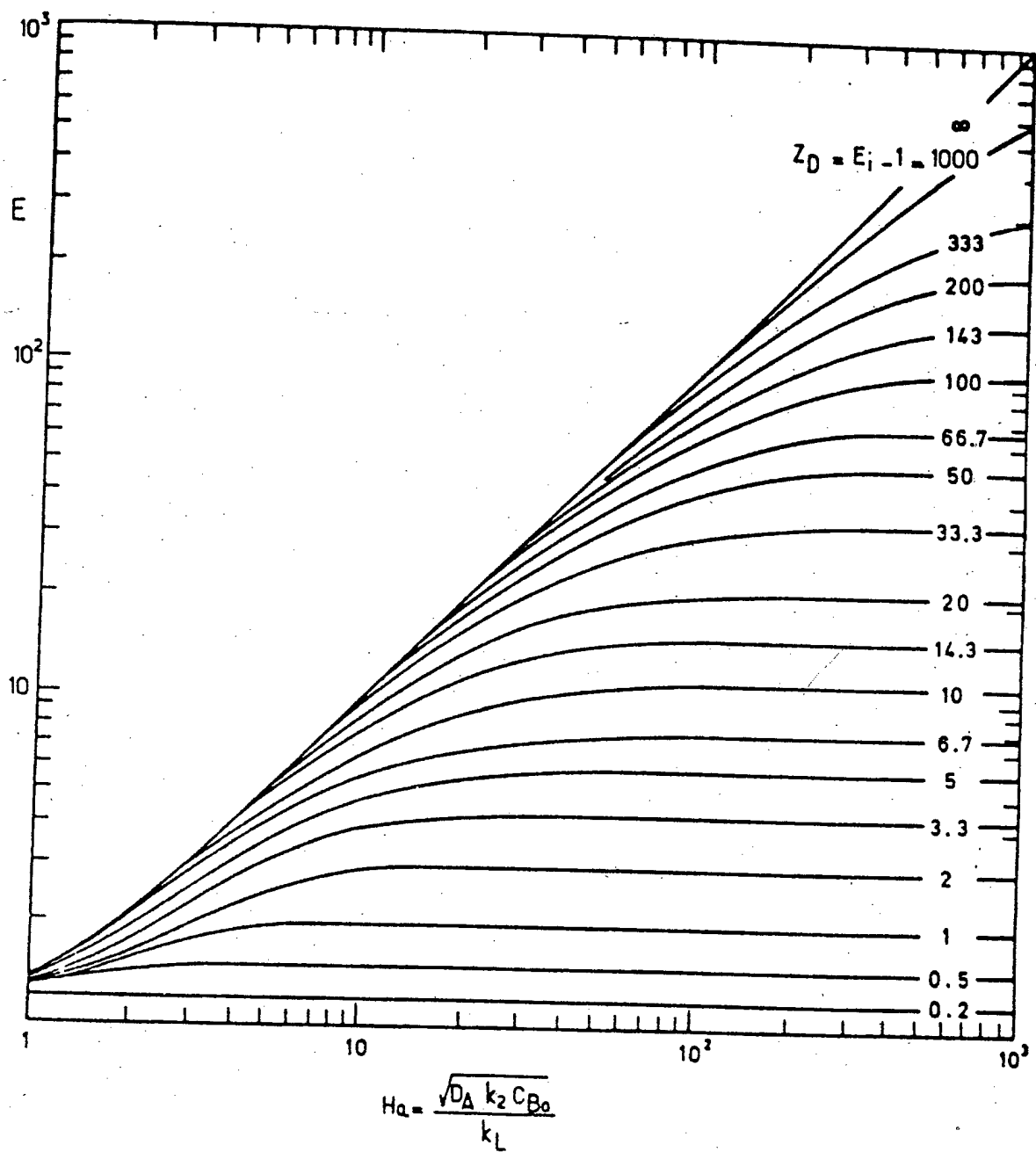


Figure A-1. Enhancement Factor for Second-Order Reaction ( $Ha > 3$ ) (Carpentier, 1981)

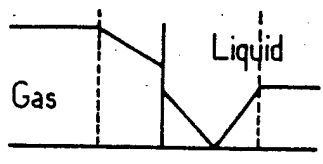
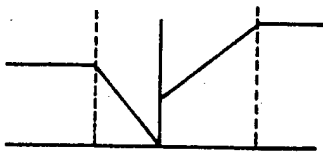
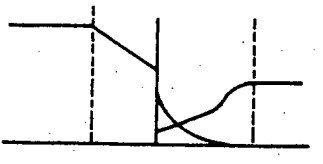
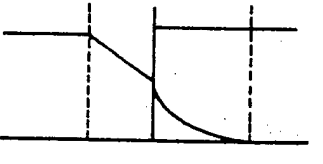
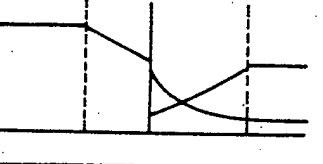
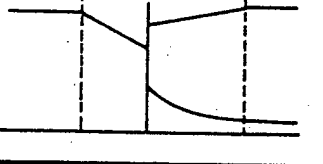
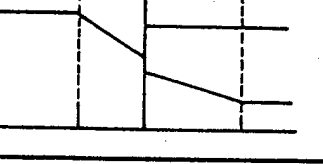
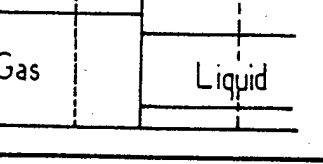
Regime	Interface concentration profiles	Rate equations	
Instantaneous		$\psi = \frac{p}{He} + \frac{D_B}{D_A} \frac{C_{B0}}{Z}$ $\frac{1}{k_L} + \frac{1}{He k_G}$	A
Instantaneous and surface		$\psi = k_G p$	B
Rapid		$\psi = \frac{p}{\frac{1}{k_G} + \frac{He}{E k_L}}$	C
Rapid pseudo 1st or mth order		$\psi = \frac{p}{\frac{1}{k_G} + \frac{He}{\sqrt{D_A k_2 C_{B0}}}}$	D
Intermediate		No exact general expression developed	E
Intermediate		No exact general expression developed	F
Slow diffusional process		$\psi = \frac{p}{\frac{1}{k_G} + \frac{He}{k_L} + \frac{He a}{\beta k_2 C_{B0}}}$	G
Very slow chemical process in the bulk of the liquid		$R_A = k_2 C_A^* C_{B0} \beta$	H

Figure A-2. The Interface Concentration Profiles and Corresponding Absorption Rate Forms (Carpentier, 1981)

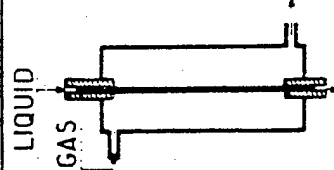
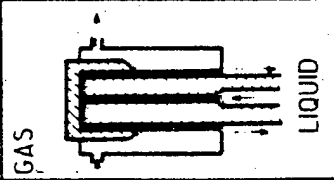
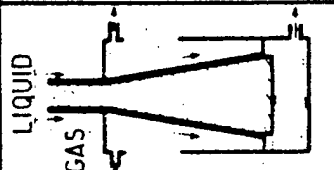
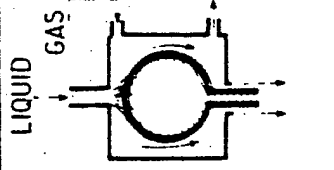
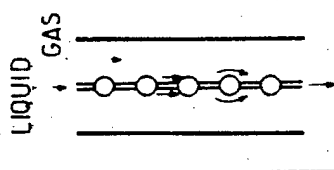
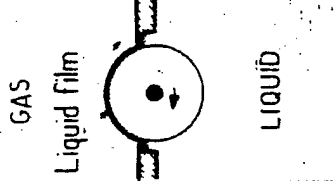
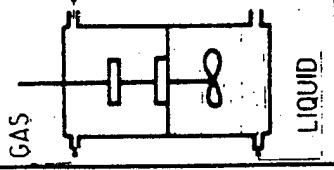
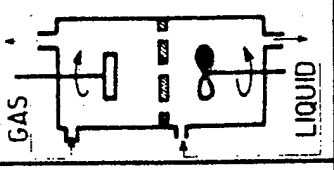
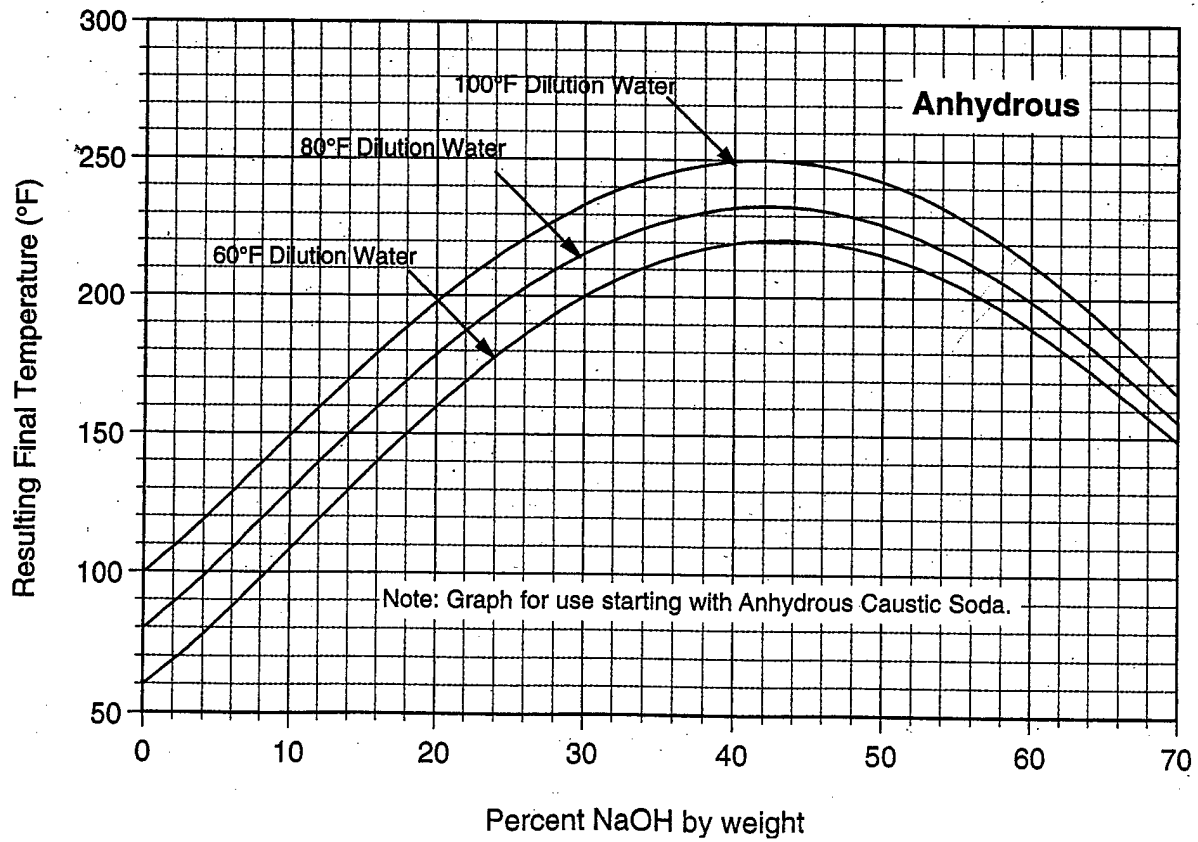
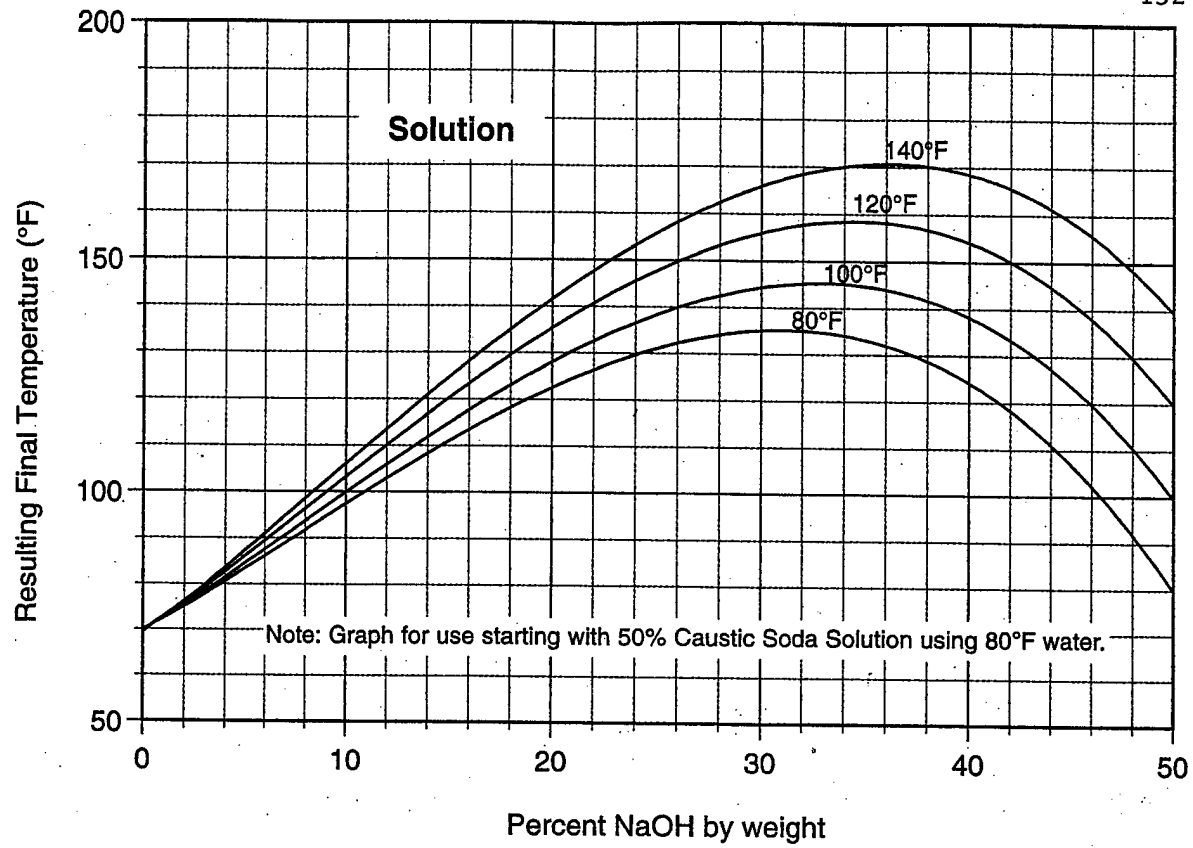
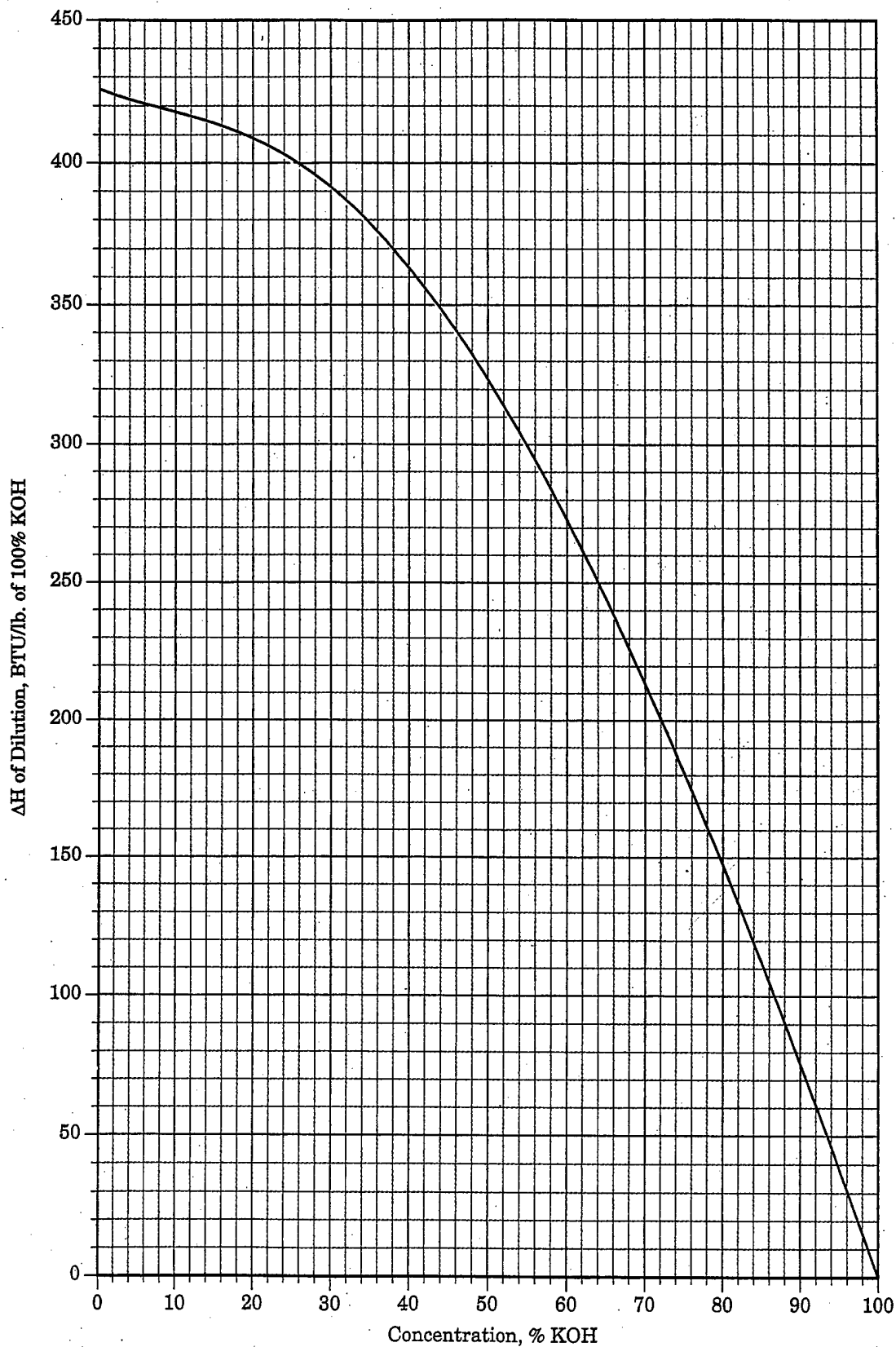
TYPE	SCHEME	LAMINAR JET	CYLINDRICAL WETTED WALL	CONIC WETTED WALL	SPHERICAL WETTED WALL	STRING OF DISKS	ROTATING DRUM	STIRRED VESSEL	STIRRED VESSEL	
										
$k_L$ cm/sec		0.016 -0.16	$3.6 \cdot 10^{-3}$ -0.016	$5 \cdot 10^{-3}$ -0.011	$5 \cdot 10^{-3}$ -0.016	$3.6 \cdot 10^{-3}$ -0.016	0.016 -0.36	$1.6 \cdot 10^{-3}$ -0.02	$2 \cdot 10^{-3}$ -0.02	
CONTACT TIMES		$10^{-3} - 10^{-1}$ sec	$10^{-1} - 2$ sec	0.2 - 1 sec	0.1 - 1 sec	$10^{-1} - 2$ sec	$2 \cdot 10^{-4} - 10$ sec	0.06 - 10 sec	0.08 - 10 sec	
INTERFACIAL AREA		$0.3 - 10$ cm <sup>2</sup> high precision	$10 - 100$ cm <sup>2</sup> high precision	$80$ cm <sup>2</sup> high precision	$10 - 40$ cm <sup>2</sup> high precision	$30 - 360$ cm <sup>2</sup> moderate precision	diameter 10cm length 12cm high precision	$80$ cm <sup>2</sup> good precision	diameter 10cm length 15cm 2-30% open	

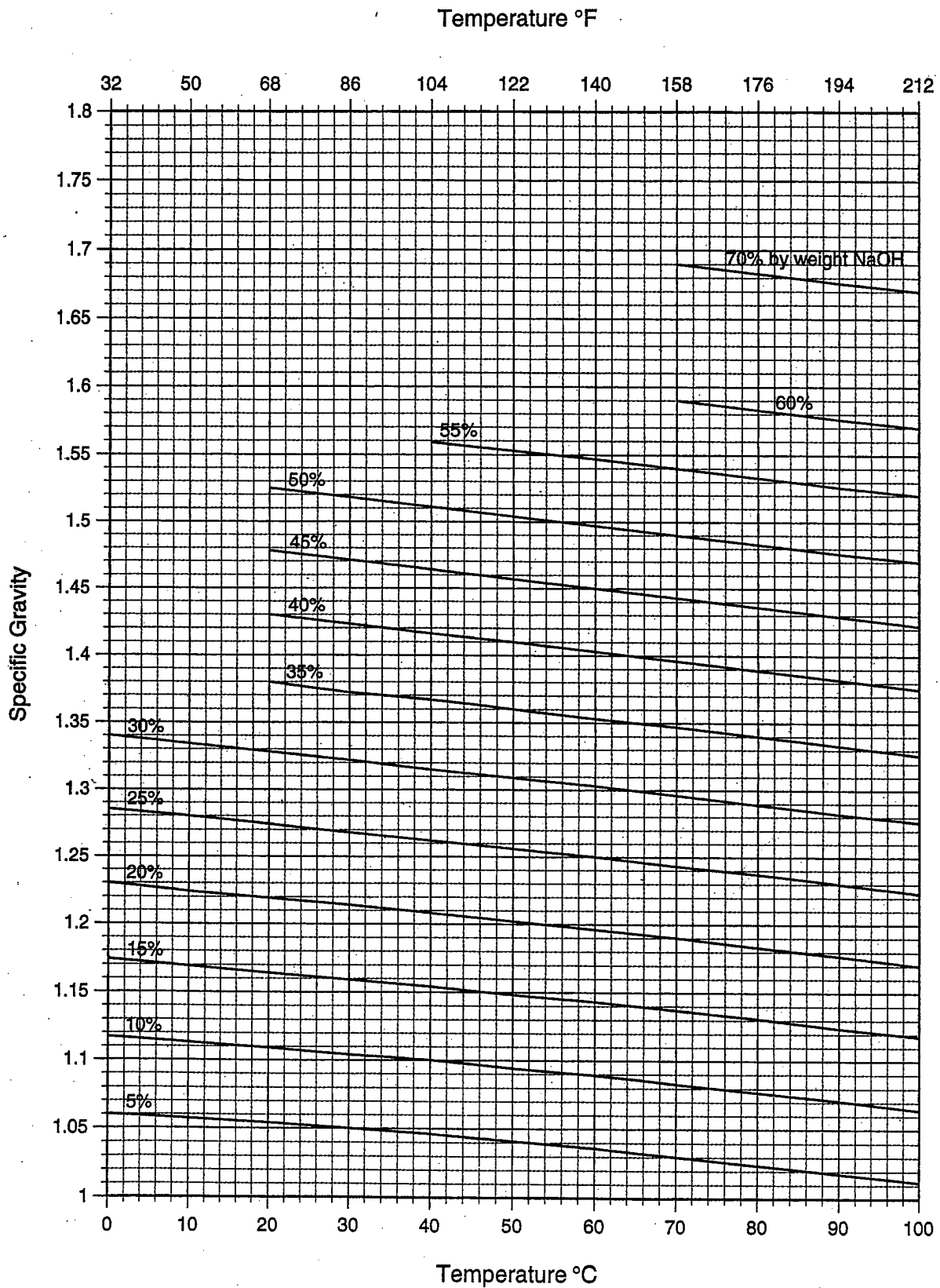
Figure A-3. Principal Types of Laboratory Techniques for Studying Gas-Liquid Reactions (Carpentier, 1981)



**Figure B-1. Approximate Resultant Temperature when Diluting Caustic Soda**  
 (Source: Occidental Chemical Corporation, Caustic Soda Handbook CV-CS-HB 2/98)

**Heat of Dilution for Aqueous KOH Solutions at 64.4°F**

**Figure B-2. Heat of Dilution for Aqueous KOH Solutions**  
(Source: Occidental Chemical Corporation, Caustic Potash Handbook EC-CP-HB 11/95)



**Figure B-3. Specific Gravity of Aqueous Caustic Soda Solutions**  
 (Source: Occidental Chemical Corporation, Caustic Soda Handbook CV-CS-HB 2/98)

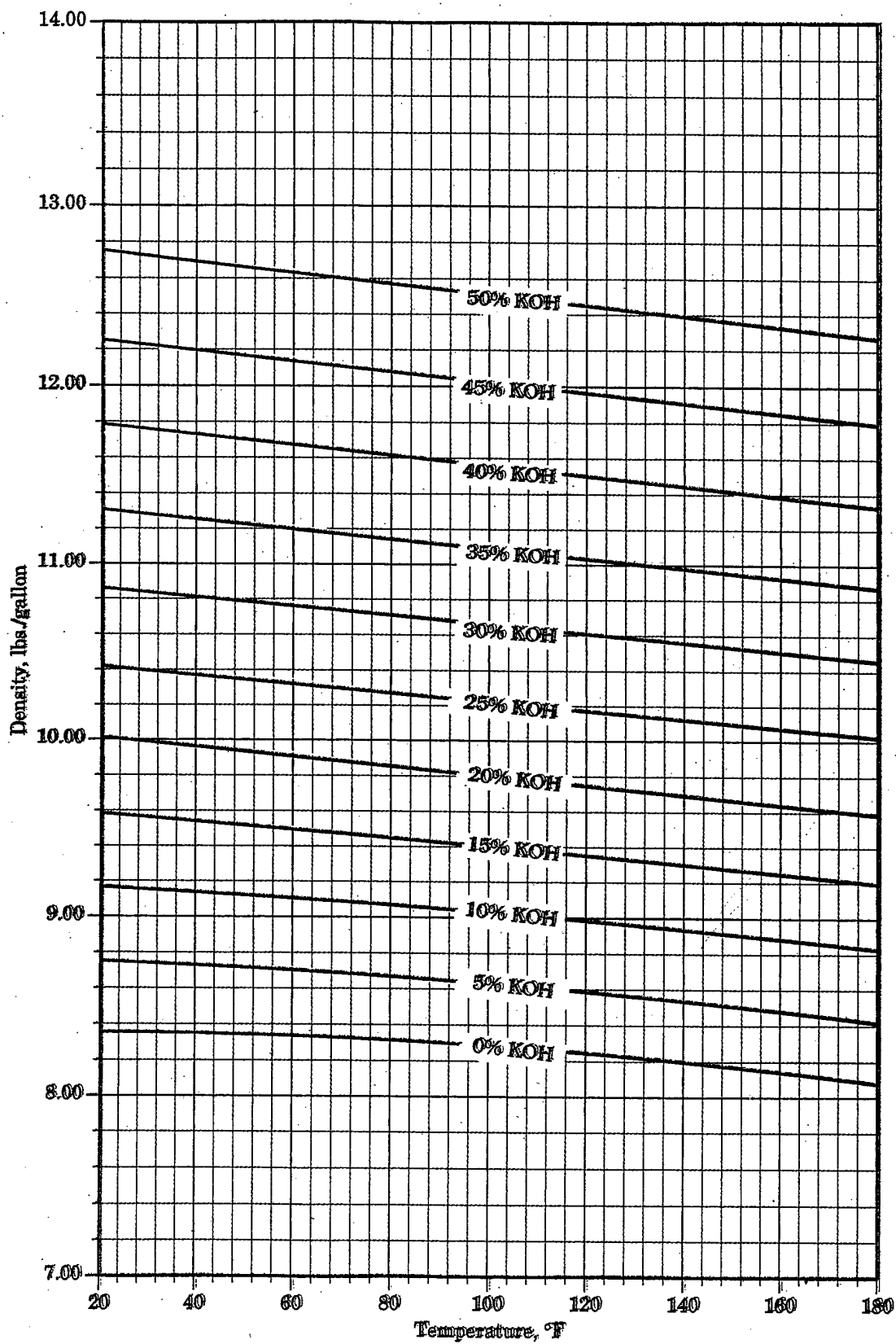
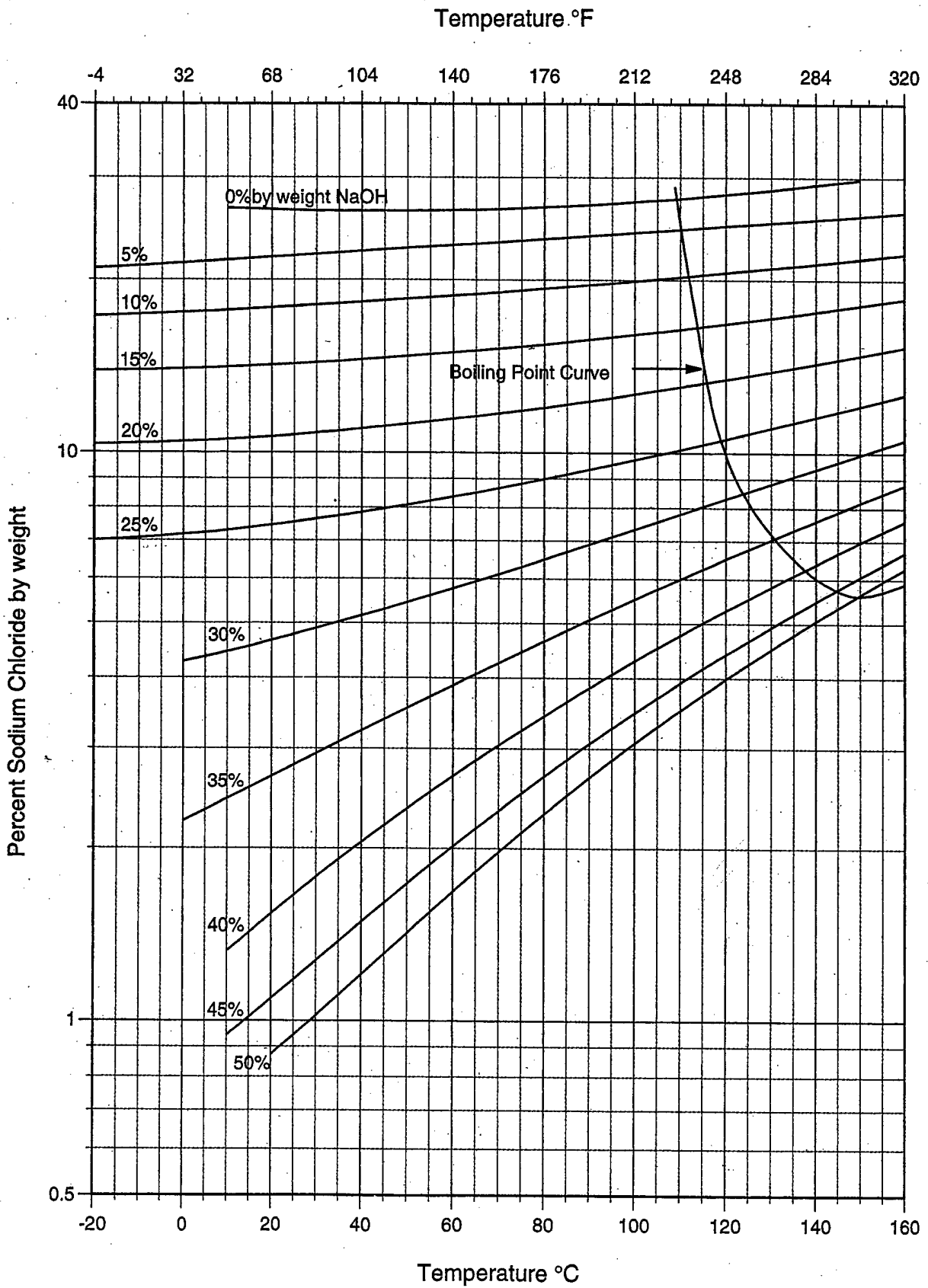
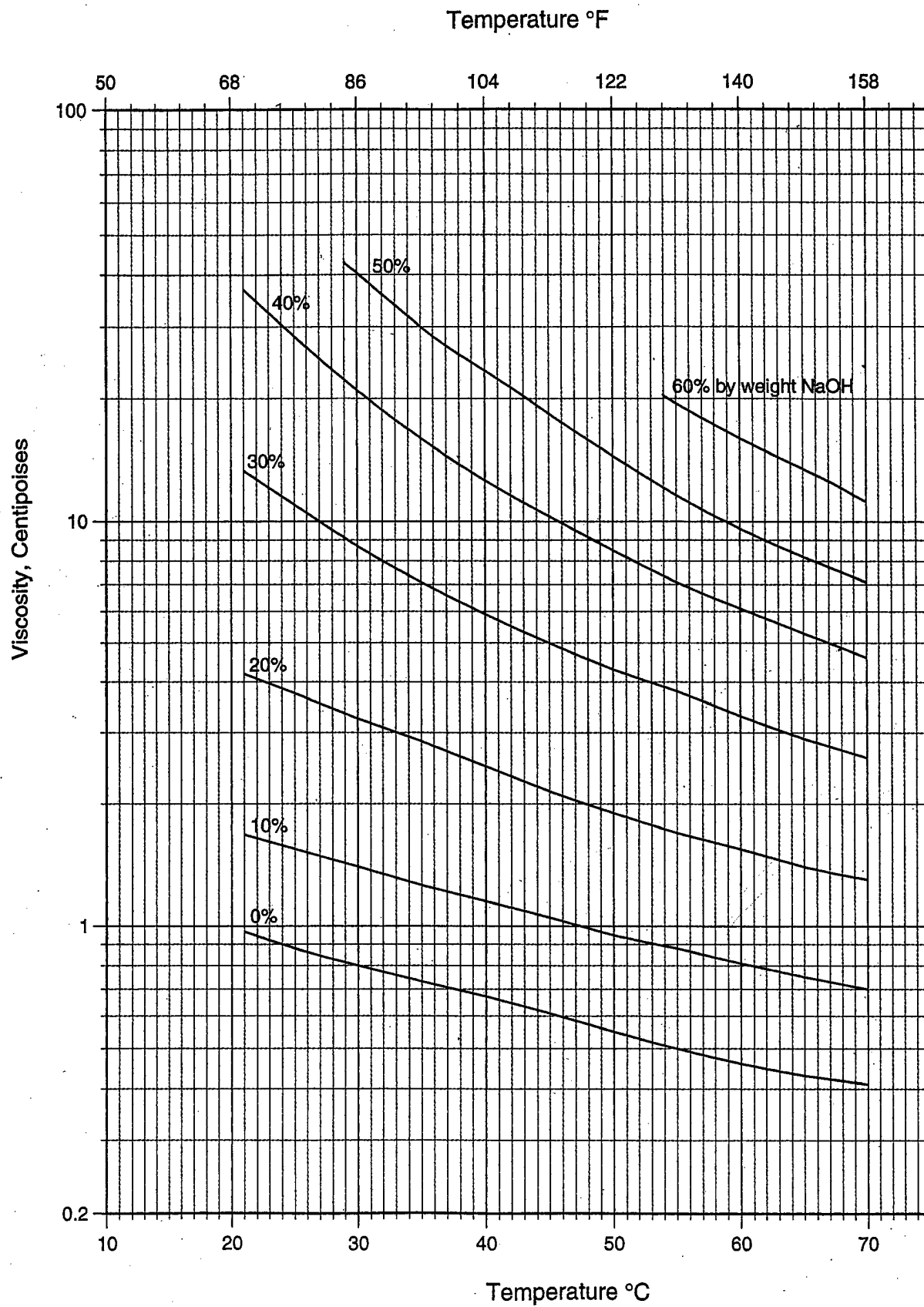


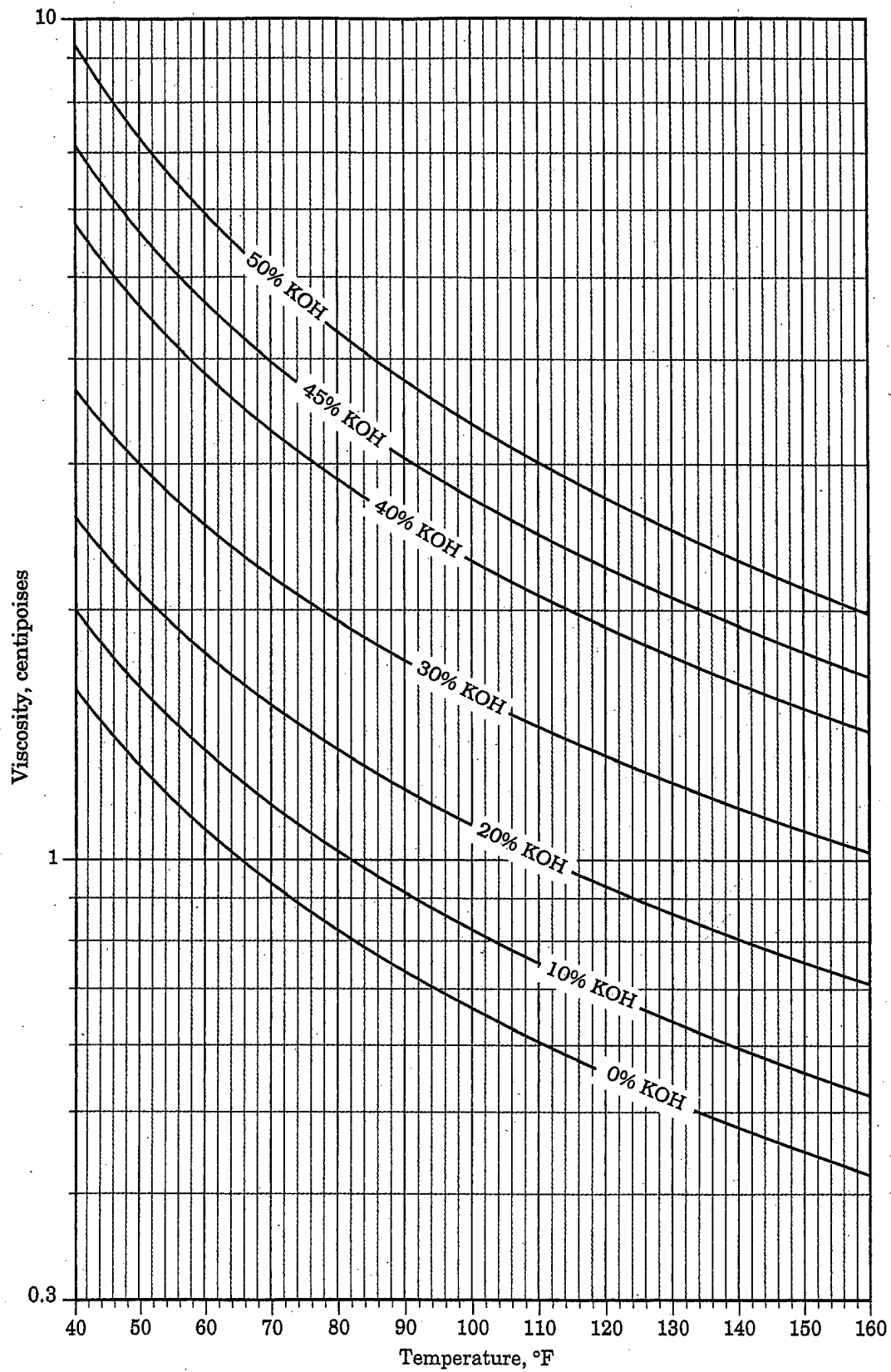
Figure B-4. Density of KOH Aqueous Solutions at Various Temperatures  
(Source: Occidental Chemical Corporation, Caustic Potash Handbook EC-CP-HB 11/95)



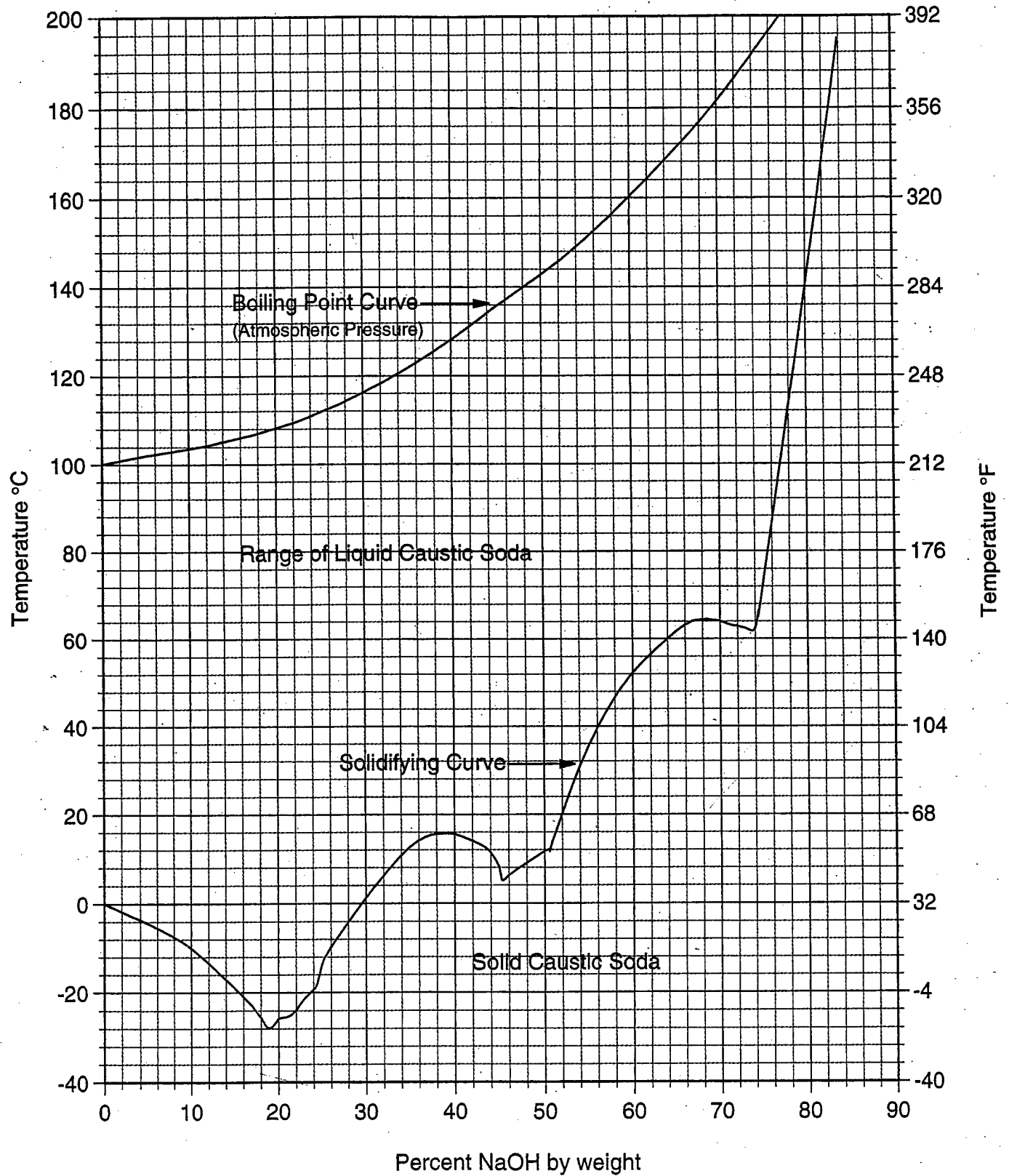
**Figure B-5. Solubility of Sodium Chloride in Aqueous Caustic Soda Solutions**  
 (Source: Occidental Chemical Corporation, Caustic Soda Handbook CV-CS-HB 2/98)



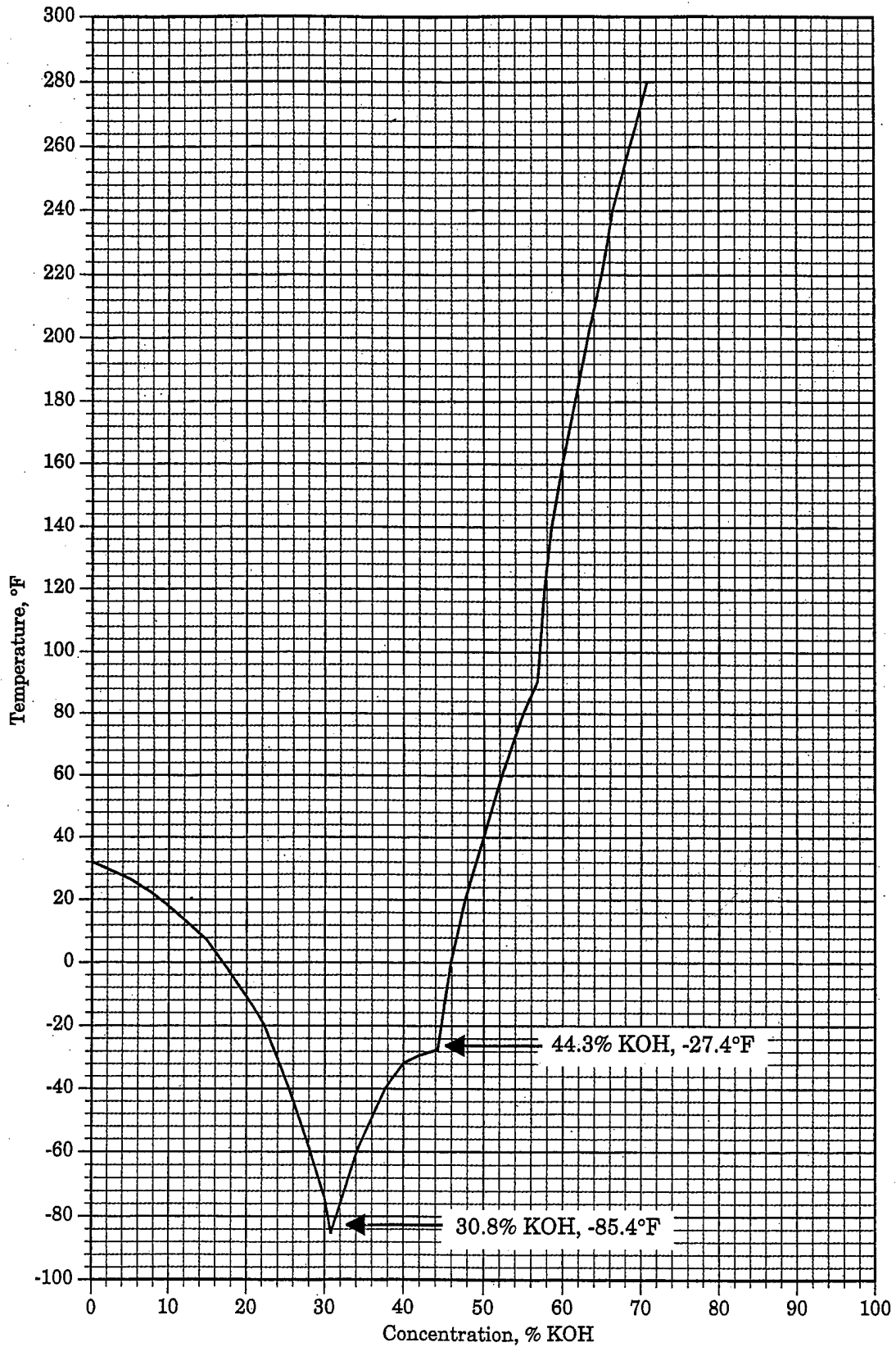
**Figure B-6. Viscosity of Aqueous Caustic Soda Solutions**  
(Source: Occidental Chemical Corporation, Caustic Soda Handbook CV-CS-HB 2/98)



**Figure B-7. Viscosity of Aqueous KOH Solutions**  
(Source: Occidental Chemical Corporation, Caustic Potash Handbook EC-CP-HB 11/95)



**Figure B-8. Boiling and Solidifying Temperatures of Aqueous Caustic Soda Solutions**  
 (Source: Occidental Chemical Corporation, Caustic Soda Handbook CV-CS-HB 2/98)



**Figure B-9. Freezing Points of Aqueous KOH Solutions**  
(Source: Occidental Chemical Corporation, Caustic Potash Handbook EC-CP-HB 11/95)

-Freezing Points of Solutions of Potassium and Lithium Hydroxides.  
Per cent. hydroxide.

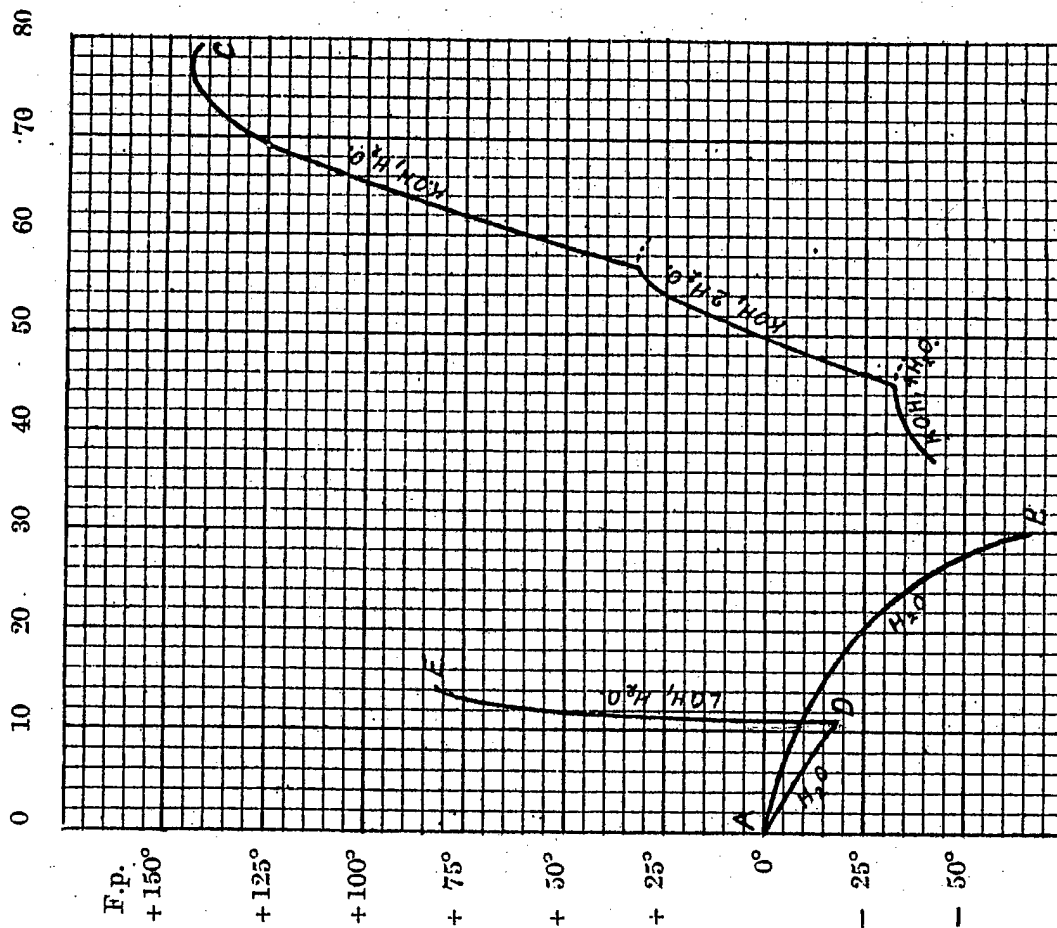
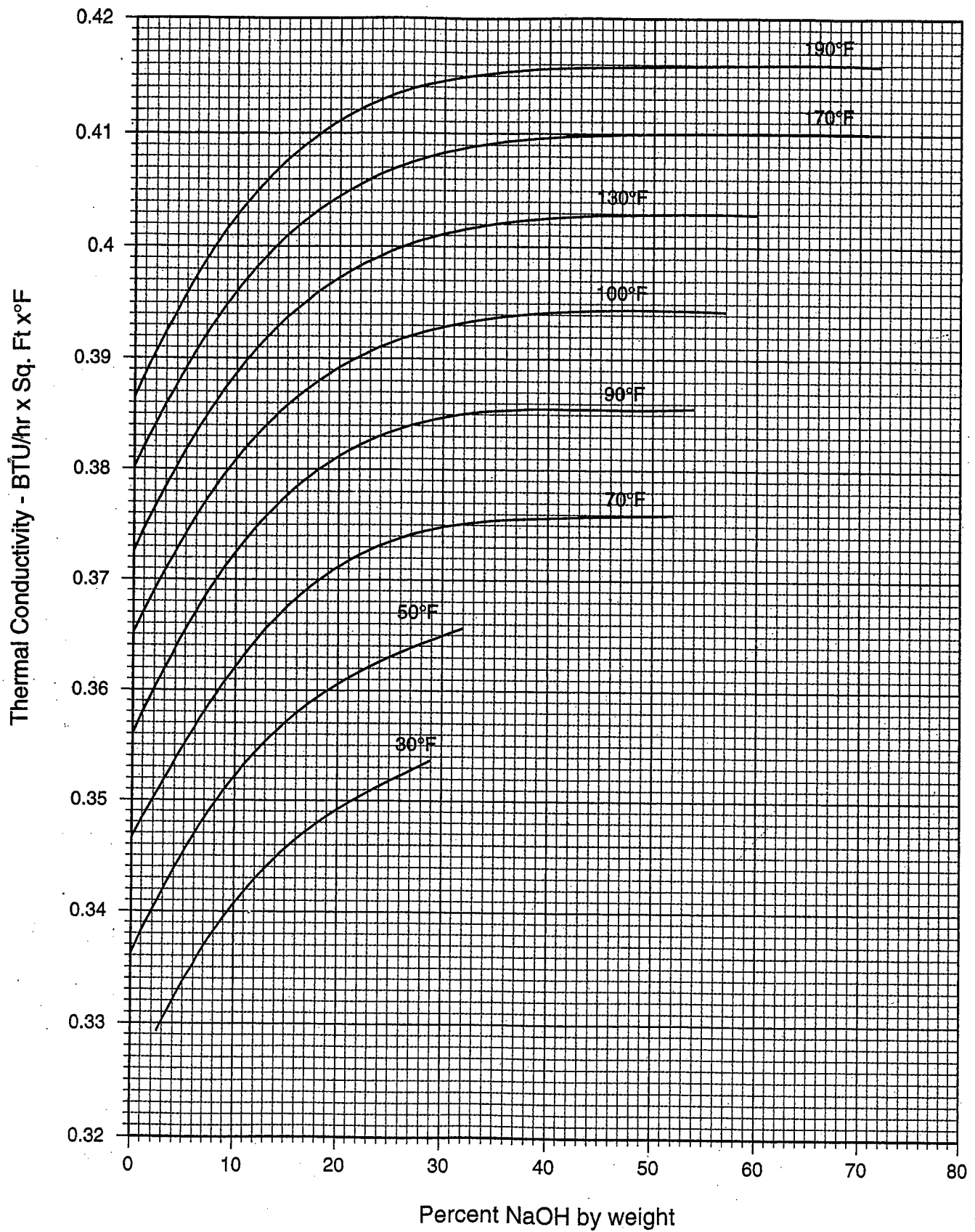


Figure B-10. Freezing Points of Aqueous LiOH Solutions (Pickering, 1893)

Per cent. LiOH.	F. P.	Per cent. LiOH.	F. P.
<i>First Series.</i>			
LiOH, H <sub>2</sub> O crystallises.			
13.20	+78.5°	13.31	+81.1°
12.60	+72.0	13.01	+77.3
11.91	+58.0	12.69	+71.85
Water crystallises.			
9.45	-14.8	12.36	+66.5
8.77	-13.4	12.03	+58.5
8.07	-12.5	11.68	+45.5
7.40	-11.5	11.36	+33.5
6.66	-10.6	11.28	+10.0
5.86	-9.5		
4.99	-7.5		
4.05	-6.0		
3.20	-4.4		
1.39	-1.85		
<i>Second Series.</i>			
LiOH, H <sub>2</sub> O crystallises.			
10.65	-17.4	10.65	-17.4
10.38	-16.75	10.38	-16.75
10.12	-16.45	10.12	-16.45
9.84	-15.6	9.84	-15.6
9.53	-14.9	9.53	-14.9
9.21	-14.18	9.21	-14.18
8.82	-13.25	8.82	-13.25
8.52	-12.95	8.52	-12.95
8.12	-12.1	8.12	-12.1
7.70	-11.45	7.70	-11.45
7.23	-10.5	7.23	-10.5
6.70	-9.7	6.70	-9.7
5.99	-8.7	5.99	-8.7
5.44	-7.8	5.44	-7.8
4.89	-6.75	4.89	-6.75
4.31	-5.9	4.31	-5.9
3.59	-4.9	3.59	-4.9
2.83	-3.8	2.83	-3.8
2.00	-2.7	2.00	-2.7
1.16	-1.5	1.16	-1.5



**Figure B-11. Thermal Conductivity of Aqueous NaOH Solutions**  
(Source: Occidental Chemical Corporation, Caustic Soda Handbook CV-CS-HB 2/98)