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ABSTRACT

The development of a process for the production of mixed potassium tetroxide and sodium peroxide is described in this report. The mixed oxide is obtained by the reaction of metallic sodium with potassium chloride at high temperature, followed by evaporation and combustion of the resultant mixture of potassium and sodium metal. The oxide contains available oxygen equivalent to 83 per cent potassium tetroxide, and is an efficient carbon dioxide absorbent. The process was carried out successfully in a pilot plant and material requirements were determined.

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INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Construction and Repair letter EN7(269)ME of 5 July 1935.

(b) Statement of Problem

2. The problem is to develop a process for the production of potassium tetroxide or a mixture of oxides with potassium tetroxide by means of the reduction of potassium salts and subsequent burning of the metal liberated.

(c) Known Facts Bearing on the Problem

3. Numerous reactions for the production of potassium salts to obtain metallic potassium have been described in the literature (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II). In most cases, the yield was low and exceedingly high temperatures were sometimes required. Potassium cannot be liberated from its salts by reduction with hydrogen or carbon, but it is reported to be possible with a few of the more active metals, such as calcium, magnesium and aluminum.

(d) Original Work Done at this Laboratory

4. Several previous reports cover other phases of the development of chemical oxygen sources. Naval Research Laboratory Report No. P-1568 of 1 November 1939 discusses the production of pure potassium tetroxide, K_2O_4 , by the oxidation of metallic potassium vapor. Due to the lack of a domestic source of cheap electrolytic potassium metal, other chemical reactions to obtain the metal have been studied and the results are given in this report.

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PART I. Experimental Studies of Reduction Reactions.

(a) Apparatus and Methods

5. The experimental set-up used for the laboratory studies was the same as described in the previous Naval Research Laboratory Report No. P-1568 and Appendix I. The potassium salt and reducing metal were placed in a small iron pot and heated to the desired temperature. An inert gas, such as helium or nitrogen, was then passed through the pot to hasten the evaporation of the metallic potassium liberated, the metal vapor passed into a burner where it was burned in air, and the finely divided oxide was electrically precipitated in a small tubular Cottrell precipitator.

6. Records were kept of materials, yields, temperatures, etc., to aid in the design of larger apparatus to carry out any reactions which showed promise.

(b) Experiments

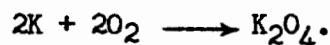
7. Potassium chloride - calcium carbide. A small yield of white powder mixed with some carbon was obtained, but the product did not liberate oxygen upon decomposition in water. It consisted largely of potassium chloride and potassium carbonate.

8. Potassium chloride - magnesium. No reaction occurred up to a temperature of 800° C. Small amounts of potassium chloride and magnesium oxide were collected in the precipitator.

9. Potassium carbonate - magnesium. A mixture of 2-3 parts of potassium carbonate with one part of magnesium turnings gave a good reaction and the product contained 88-92 per cent K_2O_4 . The oxide contained less than .5 per cent potassium carbonate, indicating that very little carbon dioxide was driven from the reaction chamber. The reaction was not complete, but it may be described approximately by the equation



Potassium metal was evaporated in a stream of dry helium and burned in air to form potassium tetroxide;



Some metallic magnesium was driven out along with the potassium, and the magnesium oxide thus produced accounted for the 8-12 per cent impurity in the K_2O_4 obtained.

10. The reaction began at about 700° C. and proceeded rapidly for a time with evolution of heat. Following the first stage of reaction, which was vigorous but not violent, the furnace temperature was raised slowly to about 760° C. Production continued for 1.5 - 2 hours, gradually

falling off, although about 40 per cent of the total yield was obtained in the first 15 minutes of reaction. It was necessary to use helium as inert gas to sweep out the potassium metal vapor. Magnesium reacts with nitrogen at high temperature, and would thus interfere with the desired reaction.

11. The yields varied from .8 to 1.1 pounds oxide per pound of magnesium used. Most of the material was yellow in color and very similar in properties to pure K_2O_4 . However, some dark gray product was frequently obtained near the end of the reaction. This was probably due to the formation of some magnesium carbide in the gaseous phase, but several closely controlled experiments failed to show what conditions caused it. Analyses showed that the darkened oxide was almost as good as the other and did not contain appreciable carbonate.

12. This reaction could be carried out on a larger scale, but there are several difficulties which would have to be considered. The required use of helium gas is objectionable, since the supply is limited. The final part of the reaction is slow, but it is necessary to continue the flow of helium to get a good yield. Another disadvantage is the fact that the residue from the reaction is still solid and cannot be tapped off as in the case of liquid residues.

13. The presence of magnesium oxide in the product leads to one drawback to its possible use. When the oxygen is to be liberated by decomposing the oxide in water, the insoluble magnesium oxide acts as a foam stabilizer and frothing is so bad that an unreasonably large container would be required. However, when it is to be decomposed by carbon dioxide and water vapor in air, as is the case when it is used in cannisters or spread out in a submarine chamber, the magnesium oxide is not objectionable.

14. Potassium carbonate - aluminum. Some reaction occurred at $780-800^\circ C$. with granular aluminum. Powdered aluminum could not be obtained sufficiently free from oil to be used successfully. In one experiment, a yield of 0.75 pound of oxide per pound of aluminum was obtained, but the product analyzed only 55 per cent K_2O_4 . At the temperature required for the reaction, potassium carbonate has an appreciable vapor pressure and the product contained about 5 per cent potassium carbonate.

15. Potassium carbonate - calcium. Practically no reaction occurred up to $780^\circ C$. At this temperature there was a violent reaction, and gray smoke was blown out. The yield was small and was not analyzed.

16. Potassium chloride - sodium. The desired reaction was the exchange of sodium for part of the potassium in the potassium chloride, according to the equation



Metallic potassium is nearly four times as volatile as sodium in the temperature range $600-800^\circ C$. It was therefore hoped that equilibrium in the

above equation could be forced to the right by evaporating off the potassium in a stream of nitrogen as it was liberated.

17. Potassium chloride was heated in the reaction chamber to about 700° C. and metallic sodium was added so that the portions were 1-3 mols potassium chloride per mol of sodium. It was found necessary to bring the mixture rapidly to 720-740° C. to get a good exchange reaction. The molten sodium had to be added before the salt melted so that an intimate mixture could be obtained and the reaction could take place rapidly. As was to be expected, the heat of reaction was small, possibly even negative, and there was no trouble with overheating. Nitrogen gas was passed through the reaction pot to speed up evaporation of the metal to be burned. A large part of the potassium liberation took place during the initial stage as the salt melted, but as the potassium was removed by evaporation further exchange occurred and the K_2O_4 content of the precipitated oxide decreased very little toward the end of a run.

18. The quality of the oxide prepared was expressed as per cent " K_2O_4 " and was determined by decomposing samples and measuring the oxygen liberated. The best mixture of reactants was found to be approximately 1.5 mols potassium chloride per mol of sodium (5 to 1 by weight). Yields of 1.8 pounds of oxide per pound of sodium were obtained, and the product was equivalent to 82 per cent K_2O_4 . Over the whole range of mixtures which were tried, the quality of the oxide produced varied only from 80-83 per cent " K_2O_4 ," but for lower proportions of potassium chloride the rate of reaction fell off rapidly. Higher proportions of potassium chloride gave the better oxide and rapid production rates, but the gain was small compared to the increased salt required.

19. The residue left was a molten mixture of sodium and potassium chlorides containing almost no free metal.

20. A further discussion of the properties of this mixed oxide will be given in the second part, in which the carrying out of this process in the pilot plant is reported.

(c) Summary

21. Of the reactions which have been considered as a possible means for producing K_2O_4 or mixed oxides containing a large proportion of K_2O_4 , two have shown promise. The reduction of potassium carbonate with metallic magnesium followed by burning of the reduced potassium yielded 90 per cent K_2O_4 . The yield was 1 pound of oxide per pound of magnesium used. There are, however, several difficulties which would hinder the carrying out of reaction on a large scale. The reduction of potassium chloride with metallic sodium followed by burning of the mixed metal formed gave a mixture of K_2O_4 and Na_2O_2 equivalent to 80-83 per cent K_2O_4 . The smoothness of this reaction and the convenient liquid form of the residue indicated that it could be readily applied to larger scale operation. Both potassium chloride and sodium are cheap and immediately available.

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PART II. Pilot Plant for Production of K_2O_4 - Na_2O_2 Mixture from Potassium Chloride and Sodium.

(a) Construction and Operation of Plant.

22. Most of the plant was the same as has been used for the production of pure K_2O_4 by the combustion of potassium vapor (Naval Research Laboratory Report No. P-1568, Part III). Aside from the reaction pot, only minor changes were made. The reaction pot was a welded steel cylinder 10 inches in diameter and 15 inches long, with 1/2 inch walls. It was supported horizontally in a furnace. Pipe connections were made into the top of the pot for introducing the potassium chloride and sodium. Pure dry nitrogen was passed through a preheater coil and into the pot through a stainless steel fitting. The nitrogen served to sweep out the metal vapor through a heated "nozzle" into the large burning chamber. At the bottom of one end of the reaction pot, a heavy steel tube was welded with a slight downward slope. This tube extended to the outside of the furnace wall and through it the molten salt residue was drained. During a run, it was plugged but at the end of a reaction, it was heated electrically and opened to draw off the residue. The plug was replaced, the heater cut off and the last of the drainings solidified in the tube to seal it. A small exhaust hood was built over the residue receiver to carry away any smoke.

23. Nitrogen was purified over heated copper and was dried by KOH and activated alumina. It was passed through a flowmeter into the preheater and reaction pot. Air was dried by KOH and either activated alumina or silica gel and then was passed through a flowmeter into the burning chamber.

24. The burning chamber and precipitator were those described in the previous report. The burner had a volume of 4.5 cubic feet and was cooled by two ordinary electric fans which helped to dissipate the heat of combustion of the potassium and sodium. The source of high d-c voltage for the Cottrell precipitator was the 500 cycle generator and transformer used with a high voltage half-wave rectifier tube. Up to 30 kilovolts were available, but operation of the precipitator seemed to be best at about 25 kilovolts. The insulation of the discharge electrode, supported from the lid of the precipitator on a 5-inch insulating rod, was improved by the use of a mica lid. The same motor driven scraper was used to clean the discharge electrode and collecting walls of the precipitator tube.

25. The plant was operated on a batch system. 10 to 16.5 pounds of potassium chloride were charged into the pot, which had been heated to 775° C. After a short time to allow the salt to heat, 2-3.5 pounds melted sodium were run in. In about 40 minutes, the mixture was hot and the reaction well along. The nitrogen was then turned on and evaporation of the metal began. Good production of oxide began at once, and the rate depended upon the temperature of the pot and the rate of flow of nitrogen. For a charge of 12.5 pounds potassium chloride and 2.5 pounds sodium, the preliminary heating required 50 minutes and the evaporation almost 2 hours. The draining and recharging of the pot required but a few moments' time.

26. The furnace heaters were automatically controlled by a recorder-controller which measured the temperature of a thermocouple inserted into a well in the pot. This temperature was maintained near 780° C. The temperature of the furnace was about 800° C. The thermocouple inside the pot was fouled, however, and for the later runs the furnace temperature measured next to the pot was controlled at 800° C. For all the runs the "nozzle" temperature was controlled at 825° C. to minimize condensation of metal at its tip.

27. The potassium chloride met the following specifications:

KCl - 98 per cent
K₂CO₃ - Not over .2 per cent
Moisture - Not over .03 per cent
Melting point - Not less than 760° C.
Free from acid or alkali.

The salt must be granular and the crystal size small. The metallic sodium was of commercial quality and was furnished in the form of clean 2-1/2 pound bricks.

(b) Results

28. The effect of the size of charge on the extent of reaction was an important factor to be determined in the pilot plant. The charge was increased to 40-50 times that used in the laboratory experiments. Several runs in which 10 pound charges of potassium chloride reacted with various weights of sodium were made to check the operation of the plant and to find what quality of oxide could be obtained. Analyses were made and are given in Table 1.

TABLE 1

<u>Run</u>	<u>Lbs KCl</u> <u>Lbs Na</u>	<u>Mols KCl</u> <u>Mols Na</u>	<u>Analysis</u> <u>% K₂O₄</u>
1	3.5	1.08	82.1
2	8.4	2.61	85.5
3	5.0	1.56	82.8
4	9.4	2.9	85.3

For similar proportions of salt and sodium, the product was of practically the same quality as obtained in the laboratory tests. It was possible to try higher proportions of salt in the pilot plant and the 85-86 per cent material was produced. The reaction proceeded smoothly and rapidly. For low ratios of salt to sodium, production of oxide was slow, but for the higher ratios production was rapid and the nitrogen consumption much less.

29. The plant was put into steady operation to produce a quantity of the oxide for testing purposes. A summary of the operating data up to the present time is given in Table 2.

TABLE 2

Run	1	2	3	4
Lbs KCl per lb Na	4.8	5.0	5.0	5.0
Yield, lbs	22.6	37.2	39.6	57.9
Lbs oxide per lb Na	1.82	2.08	1.89	2.00
Lbs oxide per lb KCl	0.37	0.41	0.38	0.40
Nitrogen per lb oxide, cu. ft.	23.9	21.9	16.0	14.1
Production rate during evapora- tion, lbs/hr.	1.47	1.52	2.06	2.24
Loss at nozzle % of yield	9.3	13.7	14.7	5.6
Analysis, % "K ₂ O ₄ "	82	--	83.0 ±0.5	--

(c) Discussion

30. The results of the pilot plant operation corresponded closely to the best results which had been obtained in the laboratory experiments. The size of charge has no effect on the course of the reaction, provided the relative area of contact between molten metal and molten salt is not radically changed. Thus, a very deep pot of small diameter would not allow much reaction between the two liquid layers after the salt had melted. Continuation of the exchange reaction after the melting of the salt undoubtedly depends upon a considerable solubility of the metal in the molten salt at the temperatures of 750-800° C.

31. The yields and quality of oxide were slightly better than for the laboratory tests. 5 to 1 charges which were mostly used gave yields of 2.0 pounds of oxide per pound of sodium used, and analyses from a number of different charges showed 83.0 ±0.5 per cent "K₂O₄." These results have been obtained during steady operation of the plant and are believed to be entirely reliable. Two charges per day of 12.5 pounds potassium chloride and 2.5 pounds sodium were usually run and the total time required was 5 hours, 45 minutes. As control of the plant was improved, the production rate increased and the nitrogen consumption was cut down.

32. The actual composition of the mixed oxide may be estimated from its analysis and the extent of the exchange reaction thereby determined. Potassium tetroxide as prepared analyzes 98 per cent K_2O_4 , while sodium peroxide prepared by burning sodium vapor is equivalent to 56 per cent K_2O_4 . The 83 per cent material produced from potassium chloride and sodium is therefore approximately $\frac{83 - 56}{98 - 56} \times 100 = 64$ per cent K_2O_4 , and 36 per cent Na_2O_2 by weight. From this composition, the mixed metal evaporated from the reaction pot is then 63 per cent potassium and 37 per cent sodium. The potassium in one pound of mixed metal is .63 pound, which is equivalent to $.63 \times \frac{23.0}{39.1} = .37$ pound sodium. Therefore 50 per cent of

the sodium went to displace potassium from potassium chloride, and the other 50 per cent was evaporated unchanged. Finally, for a 5 to 1 charge of potassium chloride and sodium, the salt residue is calculated to contain 73 per cent potassium chloride and 27 per cent sodium chloride. Recovery of the potassium chloride from this mixture may be carried out by usual commercial methods at a fraction of the original cost of the potassium chloride. Depending upon this relative cost, the number of pounds of potassium chloride charged to the production of 1 pound of oxide will be reduced from the present figure of 2.5 pounds.

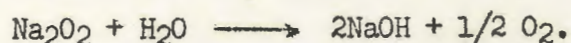
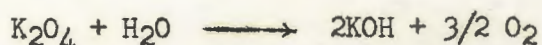
33. No unexpected troubles were found in the operation of the plant. It was dissembled after about 1 month of operation to install a cast iron reaction pot. There was no detectable corrosion inside the steel reaction pot. The stainless steel fitting through which nitrogen was injected was in excellent condition. The nozzle tip held up better than had been expected. 8 to 12 charges could be run before renewal was necessary. The repair took 1/2 day from operating time. The only other serious corrosion was the scaling of the outside of the steel pot and pipes at the 800° temperature required. The scaling was sufficiently rapid to cause failure of one pipe with 1/8" walls at the end of the month's operation. However, there are available numerous alloys and special cast irons which are non-scaling at this temperature, and since there is no corrosion inside the system, this item can be taken care of. At the present time a cast iron pot and pipes are being installed and are to be tested in operation.

(d) Properties of the Mixed Oxide.

34. The material has a density of about 15 pounds per cubic foot, as it is prepared and packed in cans. It is similar to pure K_2O_4 in that the density can be increased by heat treatment. A density of over 62-1/2 pounds per cubic foot was obtained by heating at $235^\circ C.$ for 18 hours and analysis of material which had been heat treated showed no loss of available oxygen. This material was very hard and probably too dense for use in cannisters. A somewhat shorter heating period gives a lower density. However, a higher temperature and longer heating is required to shrink the mixed oxide to a coherent form than is necessary for pure K_2O_4 .

35. The mixed oxide decomposes vigorously in water with liberation of oxygen according to the equations

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Catalysts such as cuprous oxide, anhydrous cupric salts, or manganese dioxide catalyze the complete decomposition in water. Easily combustible organic substances are ignited by the oxide. It is slightly more reactive than K_2O_4 in this respect.

36. More extensive tests will be made of the oxide for its application in air purification and as an oxygen source. It has already been found to be a good carbon dioxide absorbent, and the results of some tests are given in Table 3. Samples were spread out to 0.3 pound per square foot of area and exposed in a closed room held at constant temperature and humidity, and containing carbon dioxide in the air. In Test A, the room was kept at 70° F. and 80 per cent relative humidity, and the air contained 1.9 per cent carbon dioxide. In B, the room was at 37° F., 87 per cent relative humidity, and contained 2.6 per cent carbon dioxide. The material in B1 was compressed at 10,000 pounds per square inch, and crushed to pass a six-mesh screen. That in B2 was heat treated at 190° C. and crushed to pass a six-mesh screen.

TABLE 3

<u>Test</u>	<u>Material</u>	<u>CO₂ Absorbed Per Lb of Oxide, Cu. Ft.</u>			
		<u>1 hr.</u>	<u>3 hrs.</u>	<u>5 hrs.</u>	<u>7 hrs.</u>
A	Powder	2.02	3.82	4.49	4.9
B1	Pressed, crushed	0.98	2.16	2.52	2.91
B2	Heated, crushed	0.78	2.48	3.76	4.53

38. The heat treated oxide remains more porous than highly compressed material. It absorbs carbon dioxide faster and takes up a larger total volume per pound of oxide used. Oxygen was of course given off by the oxide as it was decomposed by the carbon dioxide and moisture in the air. No catalyst appeared to be required under these conditions. The mixed oxide liberates less oxygen per pound than K_2O_4 , but it absorbs as much carbon dioxide as the pure oxide. Data for pure K_2O_4 will be given in another report on its reactions along with further discussion of the results.

(e) Conclusions and Recommendations

39. A cheap domestic supply of metallic potassium from which K_2O_4 can be made is not at present available. A process has been developed for the production of mixed potassium tetroxide - sodium peroxide from the reaction between potassium chloride and metallic sodium. The reaction was first studied on a laboratory scale and then a pilot plant was set up to prepare larger quantities. The mixed oxide was produced in the pilot plant at the rate of 12 pounds per 8-hour day. The mixed oxide will liberate 3.15 cubic feet of oxygen and absorb 4.5 cubic feet of carbon dioxide per

pound. Heat treatment of the oxide at 235° C. increases its apparent density to about 60 pounds per cubic foot and converts it to a coherent form which may be crushed to the desired granular size. Approximately 175 pounds of the material are now available for test purposes.

40. It is believed that the process described in this report is applicable to large scale production of mixed potassium tetroxide - sodium peroxide. It is recommended that the material be further tested for the various uses to which it may be put as a chemical oxygen source and carbon dioxide absorbent.