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SEPARATION OF POLONIUM FROM BISMUTH BY DISTILLATION

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R. W. Endebrock
P. M. Engle

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Mound Laboratory
Miamisburg, Ohio

Technical Information Service, Oak Ridge, Tennessee

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THE SEPARATION OF POLONIUM FROM BISMUTH BY DISTILLATION

(Information Report)

BY

R. W. ENDEBROCK AND P. M. ENGLE

Date: August 1, 1953

Work performed under Contract No. AT-33-1-Gen-53

MOUND LABORATORY
Operated by
Monsanto Chemical Company
Miamisburg, Ohio

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ABSTRACT

The experimental work on the separation of polonium from bismuth by distillation during the period from 1949 to 1952 is reviewed. Data are presented showing operation of simple batch stills and of fractionating stills with and without helium sparging. The problem of materials of construction is discussed and data obtained while working on this phase of the project are included. Some of the problems of still design and construction are presented with recommendations for their solution.

INTRODUCTION

The investigation of separation of polonium from bismuth by distillation has progressed to the point where a prototype model of a still is under construction. At this point it seems appropriate to review the results of experimental work to date, much of which has been reported previously in abstract or progress-report form. The work reported in detail here is for the most part that of the Chemical Engineering Section and references are given to related work by other groups.

This work, which has been known as the Bismuth Distillation Project, has covered two general approaches to still operation; namely, simple distillation and fractional distillation. Both of these are batch processes and most of the work has been directed to fractionation. In addition, both this Laboratory and Battelle Memorial Institute have done considerable work on the corrosion of materials of still construction by heated bismuth. The details of still design necessary to obtain efficient, dependable operation have been studied carefully.

RESULTS OF EARLY DISTILLATION EXPERIMENTS

The original pilot experiments which were performed in glassware have been adequately reported.[1] The best results were: depletion of 16 grams of irridated bismuth in the still-bottom of 98.3 per cent of its polonium in 28 hours, and 99.47 per cent in 42 hours; with polonium product concentrations of 35 and 25 times that of the original charge.

FRACTIONATING STILLS

A rather large Inconel fractionating still similar to that shown in Figure 1 was constructed. Before experiments with active bismuth were started in this unit, it was found that the Inconel was attacked by bismuth to such an extent that the unit was not usable.[2] This experience emphasized the need for better information on the corrosive effects of bismuth.

A still of the same design was then constructed of SAE 1020 steel and operated with active bismuth.[3] One complete run of four cycles totalling 15½ hours was made and the data for this run are tabulated in Table I. During the second run with this equipment the still bottom failed by distortion from atmospheric pressure on the relatively-thin low-carbon steel still walls. This material has a very low creep-strength at the temperature employed, 825 °C. The data indicate a high concentration factor but a rather low rate of product recovery. These results are probably due to the long narrow shape of the still column compared to that of the still bottom.

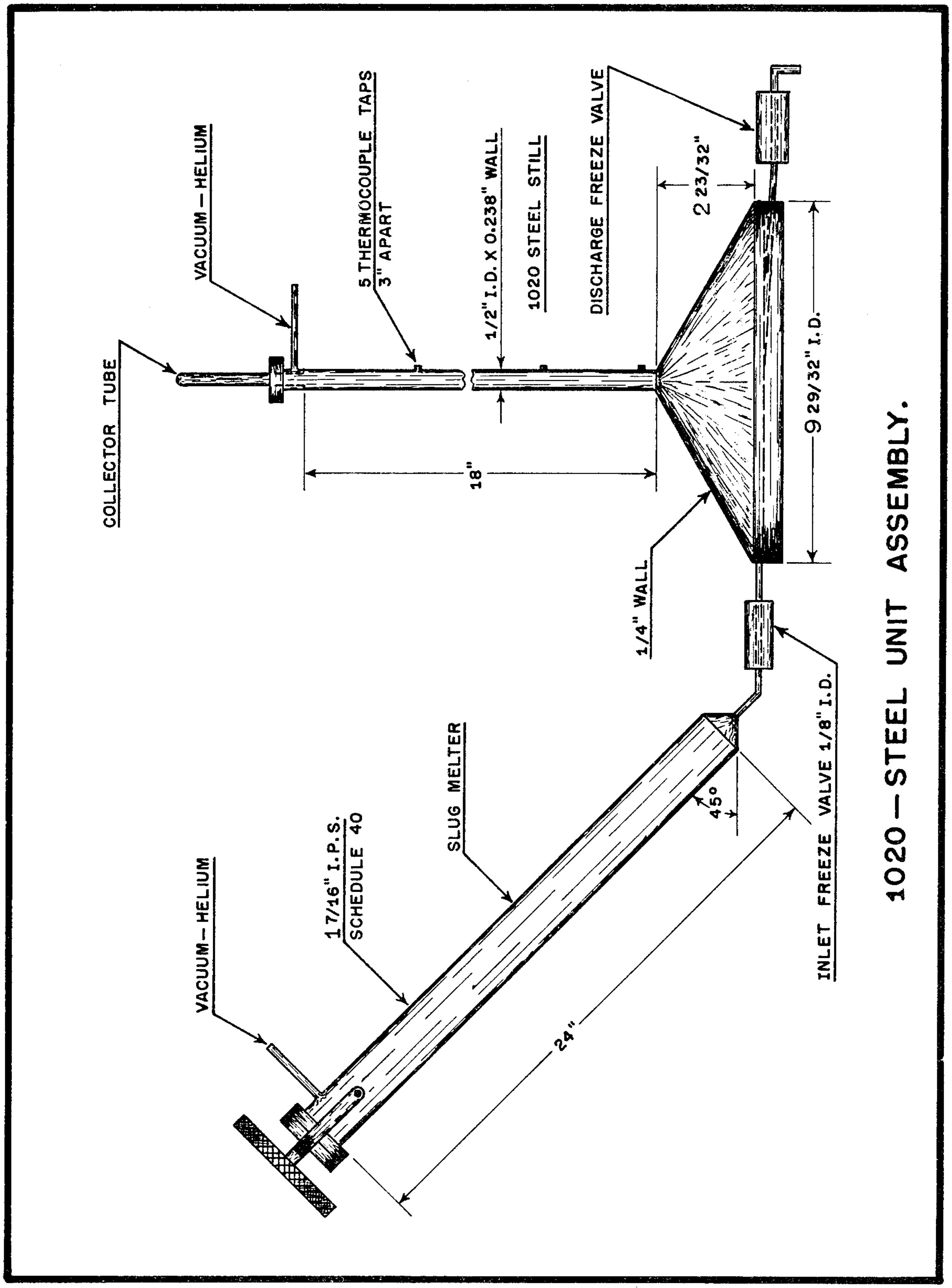

1020—STEEL UNIT ASSEMBLY.

FIGURE 1

TABLE I

SUMMARY OF DATA, SAE 1020 STEEL FRACTIONATING STILL

INITIAL CHARGE: 2,488 g Bi; 11.76 C Po

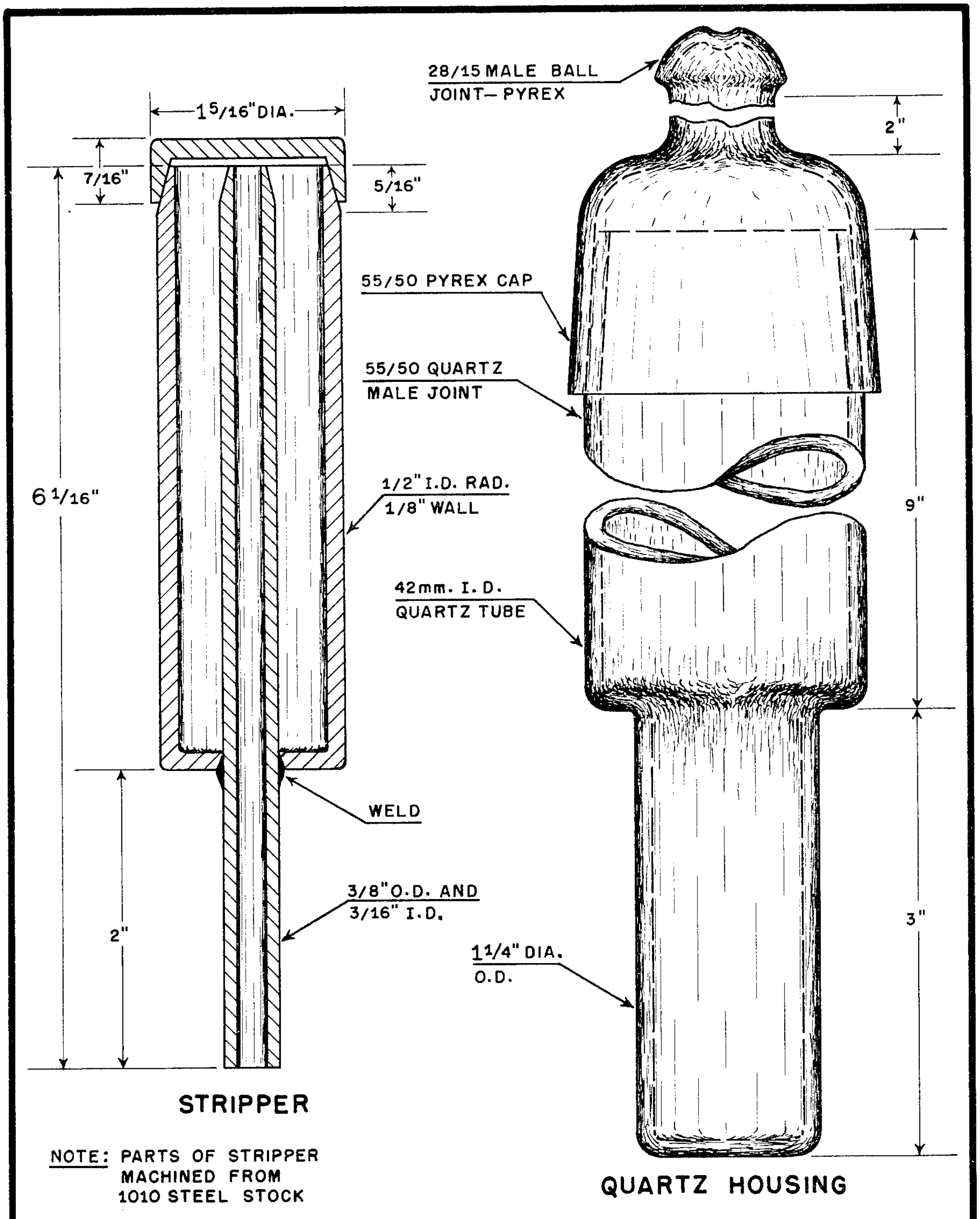
CYCLE NUMBER	RUN TIME	PRODUCT		RECOVERY		CONCENTRATION FACTOR	
		Bi	Po	CYCLE	CUMULATIVE	CYCLE	CUMULATIVE
	(hr)	*(g)*	*(C)*	*(%)*	*(%)*		
1	3.5	0.212	3.63	30.9	30.9	3625	3625
2	5.0	0.288	4.64	39.4	70.3	4920	3510
3	4.5	0.535	1.27	10.8	81.1	1692	1950
4	2.5	0.380	0.19	1.6	82.7	561	1455

NOTES: STILL BOTTOM OPERATING TEMPERATURE, 825°C.
OPERATING PRESSURE, 1 - 8 MICRONS

STRIPPING STILL

In order to demonstrate that irradiated bismuth could be depleted of its polonium content at a rapid rate by distillation, the stripping apparatus shown in Figure 2 was constructed.[3] The irradiated bismuth charge was placed in the annulus formed between the steel outer wall and the central tube. The steel assembly was capped loosely and placed in the quartz housing. The housing was evacuated and the upper four inches of the steel stripper heated to about 1000°C by induction heat. Vaporized bismuth and polonium passed upwardly through the annulus and downwardly through the central tube to be collected in a small collector tube (not shown in Figure 2) in the cooled bottom of the quartz housing. After each heating cycle the collector was removed and the product was analyzed for polonium and bismuth. The results of a run consisting of 11 cycles are given in Table II. It was demonstrated that under sufficiently severe conditions bismuth can be depleted of its polonium content rapidly by distillation. The high temperature and absence of any fractionation or partial condensation effect resulted in large amounts of bismuth being present in the products and low concentration factors were obtained.

The rates of depletion for the various early experiments are shown in Figure 3, and Figure 4 shows the variation in concentration factor and degree of product collection obtained in these experiments.



NOTE: PARTS OF STRIPPER MACHINED FROM 1010 STEEL STOCK

STRIPPER WITH QUARTZ HOUSING.

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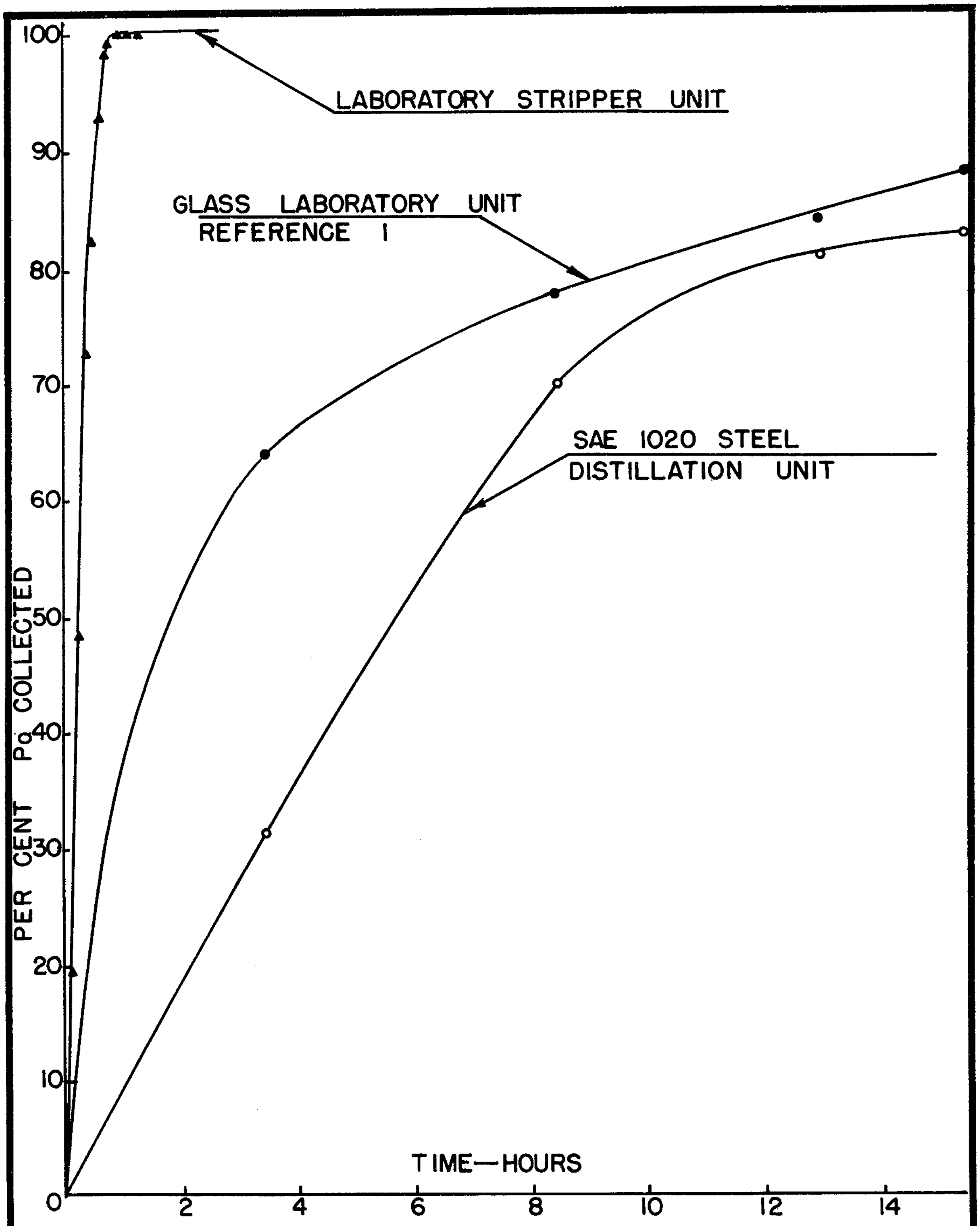
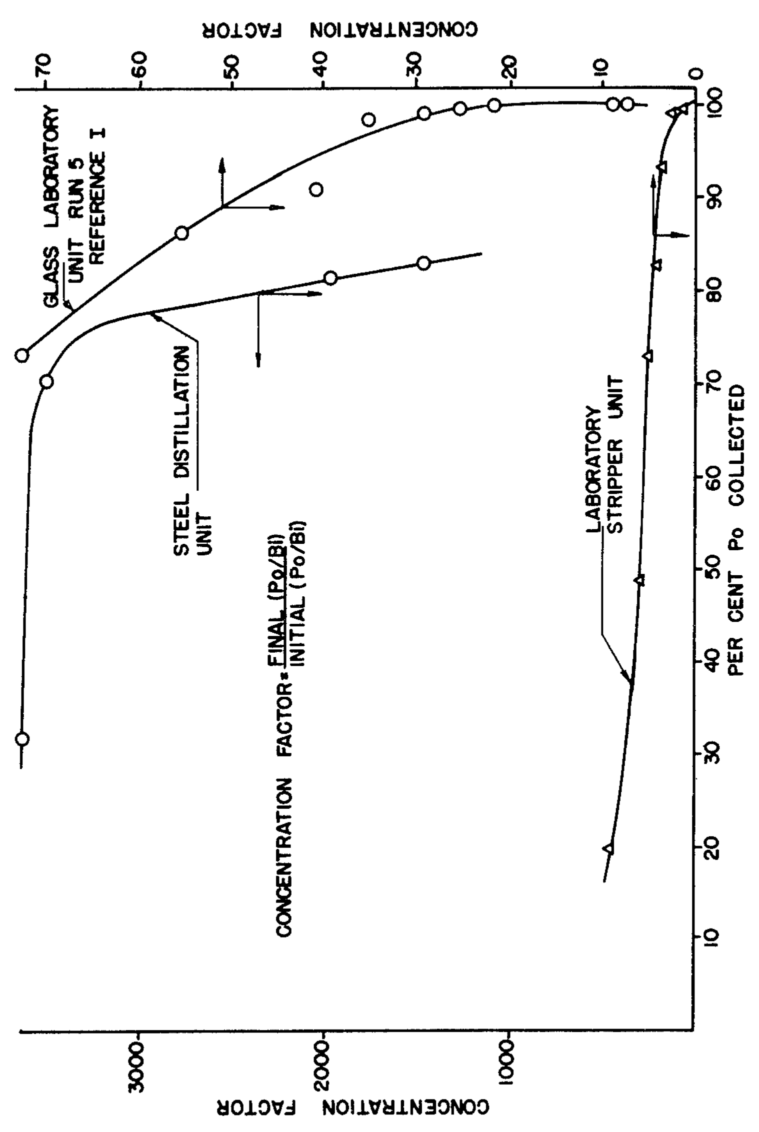
FIGURE 2



Bi-Po DISTILLATIONS CUMULATIVE % Po COLLECTED vs TIME

FIGURE 3



Bi-Po DISTILLATIONS CONCENTRATION FACTOR vs % Po COLLECTED

FIGURE 4

TABLE II

SUMMARY OF DATA, STRIPPING STILL

INITIAL CHARGE: 215.8 g Bi; 2.001 C Po

CYCLE NUMBER	RUN TIME (*Min*)	MAX TEMP (°C)	COLLECTED Po (C)	CUMULATIVE Po (%)	COLLECTED Bi (g)	CUMULATIVE Bi (%)	CONCENTRATION FACTOR	
							CYCLE	CUMULATIVE
1	6	850	0.3900	19.49	5.0376	2.33	8.33	8.33
2	8	1,025	0.5812	48.54	12.1347	8.15	6.27	6.10
3	8	986	0.4792	72.49	13.3108	14.3	6.94	5.13
4	8	1,025	0.1961	82.30	11.2821	19.6	5.86	4.26
5	9	1,070	0.2089	92.74	15.3197	26.6	6.69	3.51
6	7	1,072	0.1162	98.55	18.6803	35.4	6.76	2.81
7	4	>1,000	0.0224	99.67	21.0562	45.1	4.74*	2.22
8	7	>1,000	0.00485	99.91	22.4086	55.5	3.39*	1.81
9	8	>1,000	0.00154	99.98	20.1744	64.8	2.69*	1.55
10	7	>1,000	0.000177	99.998	22.4900	75.4	- *	1.33
11	6	>1,000	0.0000261	99.999	13.4590	81.5	- *	1.23

NOTES: PRESSURE WAS APPROXIMATELY 1 MICRON AT START OF EACH CYCLE.

*VALUES ARE NOT ACCURATE BECAUSE OF LOSS OF SIGNIFICANT FIGURES IN CALCULATION.

$$\text{CONCENTRATION FACTOR} = \frac{\text{INITIAL } \dfrac{\text{g Bi}}{\text{C Po}}}{\text{COLLECTED } \dfrac{\text{g Bi}}{\text{C Po}}}$$

AGITATION

Various methods were considered for improving still performance obtained in the early experiments. One of the most promising methods appeared to be that of agitation of the bismuth pool in the still bottom. Since the rate of polonium volatilization from the surface of the bismuth should be very rapid at the temperatures employed, it was assumed that the rate-controlling mechanism was the rate of diffusion of the polonium from the body of the melt to the surface. Experimental work described below under the heading Simple Distillation Experimental Work confirmed this assumption, at least to a degree. Several methods of ordinary mechanical agitation were investigated briefly, but these methods were not considered to be practical because of high still-temperature and vacuum requirements.

Some of the early work on distillation of polonium from irradiated bismuth indicated that small quantities of a gas or gases were liberated during distillation. Verification of this observation was made and the gases were studied at this Laboratory and at Battelle Memorial Institute.[4] The effect of liberation of gas during distillation was studied and it appeared to be beneficial. It was eventually incorporated in the design of distillation units having sparging inlets.

AGITATION TEST UNITS

Two test-units were constructed for the purpose of investigating the effect of agitation of the bismuth upon distillation.[5] One of these stills was a cylindrical unit divided into four compartments, each compartment of which was equipped with a separate identical product collection tube. After the first compartment was loaded it acted as a control means so that distillation occurred without agitation. By manipulating the pressures in each compartment, the bismuth was sprayed completely into each successive compartment. The distillation rate, expressed in millicuries of polonium per minute, was compared for each compartment. Depletion was not an important factor since the overall percentage of polonium distilled was small. The results are shown in Table III.

TABLE III

DISTILLATION RATE

COMPARTMENT	RATE (*mC/min*)
1 (NO SPRAYING)	0.74
2 (SPRAY)	17.60
3 (SPRAY)	2.90
4 (SPRAY)	12.00

This test showed a maximum distillation rate 24 times greater than the rate without agitation, and an average distillation rate 15 times greater than that without agitation. The increased surface caused by the spraying would, however, account for a portion of this increased rate.

The other still was constructed from a Pyrex cylinder having a fritted Pyrex disk sealed in the bottom. Helium was passed through the disk and into the molten bismuth causing gas agitation or sparging. A pressure of approximately 10 microns above the bismuth permitted sufficient gas to flow into the bismuth so as to give a gentle agitation. The bismuth was heated by an induction heater which caused the metal to be heated to a higher temperature than the glass still. The method of product collection proved to be subject to a variety of errors. However, based on bismuth depletion rather than product recovery, the data shown in Table IV were obtained.

TABLE IV

RESULTS OF TEST OF STILL

Po IN CHARGE - 1.480 C	DEPLETION - 71.8%
Po REMAINING - 0.418 C	DIST. RATE - 17 MC/MIN

DIST. TIME - 60 MIN

Here again a rather high distillation rate was obtained. In another test employing a fritted Pyrex disk, it was found that the rate of polonium recovery when helium was being sparged was four times that without sparging.[4] In these tests, however, the agitation was exceedingly gentle as compared to the violent agitation and increased surface area caused by spraying. The optimum flow of helium needed to maintain a maximum distillation rate has not been established. At very low sparging rates the surface of the molten bismuth is not preceptibly broken, consequently there is doubt concerning the mechanism involved in the introduction of helium to the bottom of the bismuth melt. The mechanism may be a diffusional process rather than a true agitation or may be similar in nature to steam distillation. The results of later non-sparging runs with the sparging still cast some doubt on the efficiency of sparging. Further investigation of the effect is warranted.

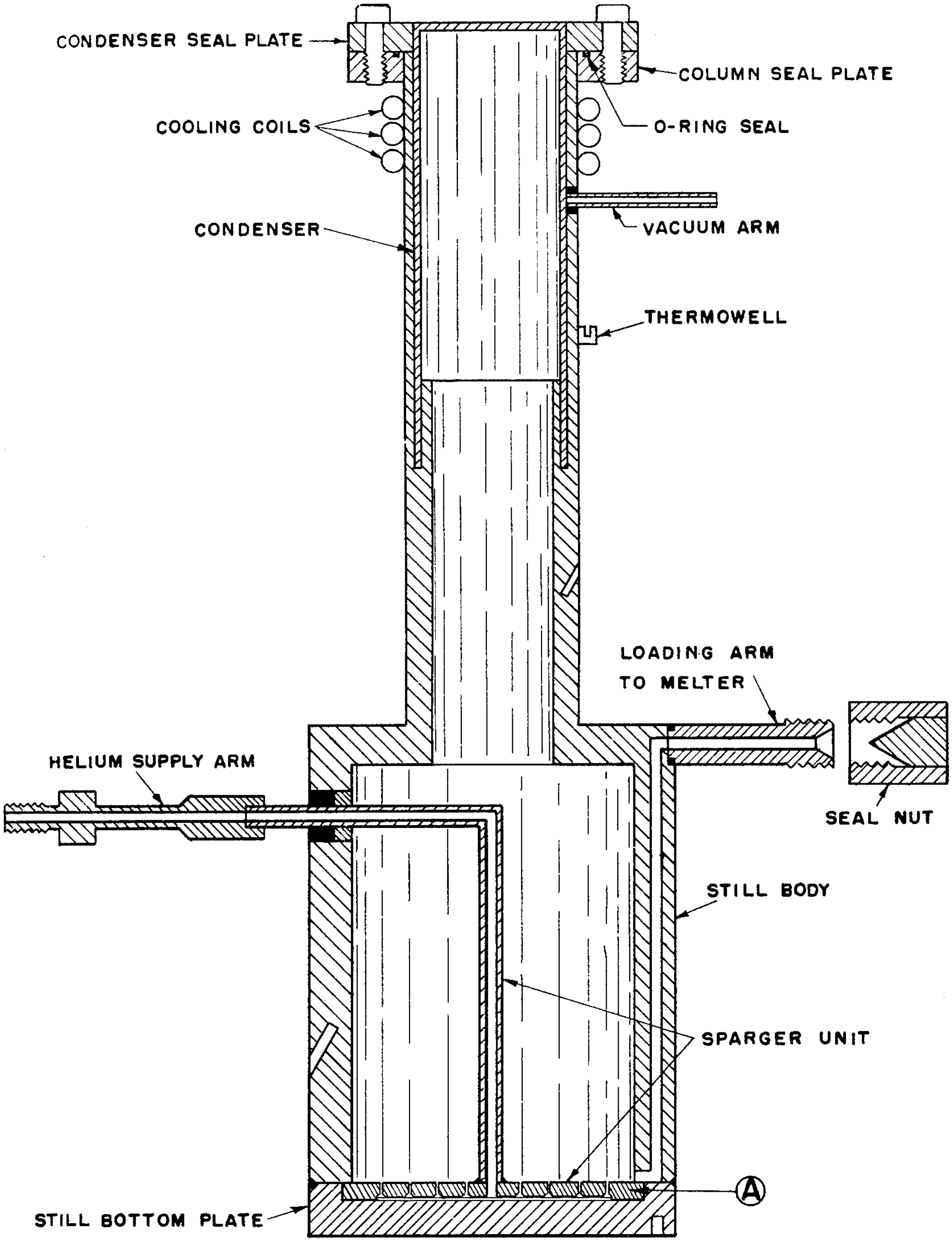
EXPERIMENTAL SPARGING STILLS

Two fractionation units with inlets for helium sparging were constructed as shown in Figure 5, one of low-carbon steel and the other of 3 per cent silicon transformer steel. Both units were operated successfully for several hundred hours and considerable design data and operating technique were obtained.

OPERATING PROCEDURE

An irradiated slug of bismuth was calorimetered and used as a still charge. The weighed charge was loaded into the still from a melter and a small quantity of non-irradiated bismuth was used to seal the loading arm. The unit was then cooled and the condenser was inspected for spattering. If spattered metal was evident it was removed and assayed for bismuth and polonium. The still was brought to temperature in approximately one hour. An initial pressure reading was taken before sparging was begun and an initial pressure of less than one micron during heat-up indicated that the vacuum system was tight. This pressure reading served as a reference value for control of sparging rate. The sparging rate was adjusted to allow an increase of 2 to 5 microns in the pressure reading, and this rate was maintained throughout the run and during the cool-down period. When a temperature of 300°C had been reached by the still pot sparging was discontinued. Pressure readings were taken until the still temperature was below 200°C.

After the still had cooled the product condenser was removed and inspected for signs of oxidation which was indicated by discoloration of the condenser. An inspection for the presence of polonium on the outside surface of the condenser was made with zinc sulfide paper to make sure that complete colleotion had occurred on the inside surface. No appreciable outside contamination was found during the runs. The product was then carefully dissolved in concentrated nitric acid, placed in a new 100-milliliter volumetric flask and adjusted to a



SPARGER STILL

FIGURE 5

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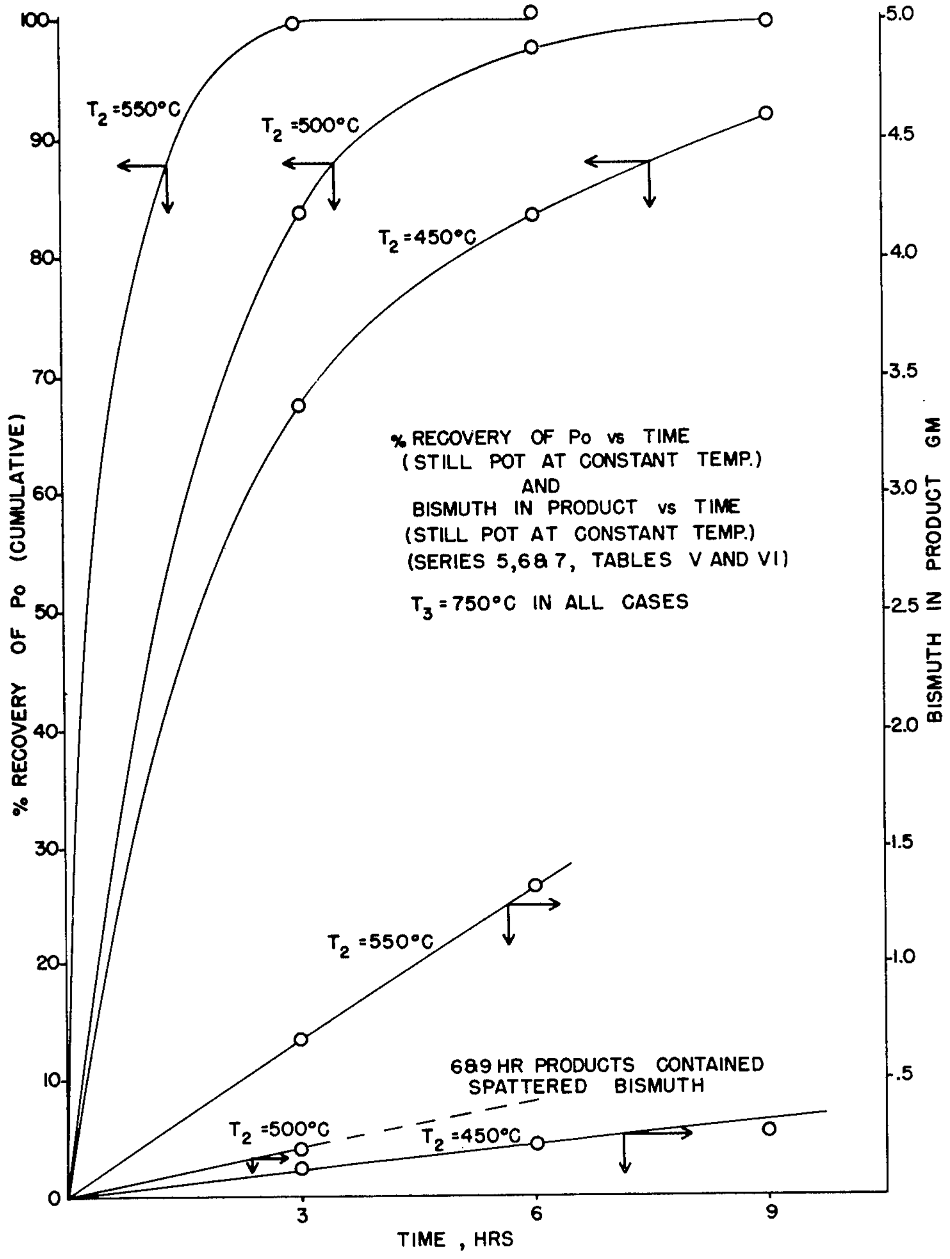
concentration of approximately four-normal with nitric acid. A sample was sent to the Micro-Assay Group for determination of bismuth, and a second sample was mounted with special precaution being exercised to maintain clean micro-pipettes. This mount was counted. Every effort was made to keep counting errors at a minimum, and known samples were frequently counted as control blanks. As a result of these precautions, material balances were generally well within counting error. The still was unloaded, the spent bismuth was weighed, and a small sample of the bismuth weighing one to three grams was dissolved in 100 milliliters of four-normal nitric acid. A sample of this solution was mounted and counted. Again precautions were exercised to obtain reliable results. An assay of the spent bismuth provided a method for cross-checking the recovery, and was subject to less error than an assay of the product solution. Large percentage errors in counting low-activity solutions gave less overall error in material balances than small errors in counting of high-activity product solutions. A weighed sample of the dissolved spent bismuth was sent to Micro-Assay Group as a control-check on the thiourea colorimetric method used for the determination of bismuth in the product.

LOW-CARBON STEEL SPARGING STILL

Data obtained from the low-carbon steel unit included: (1), optimum operating temperatures of the column and still-bottom for a three-hour cycle; (2), the general effects of variations of column and still-bottom temperatures on distillation; (3), partial data on the effect of column constrictions; and (4), partial data on the effect of variations in bismuth-depth on performance.

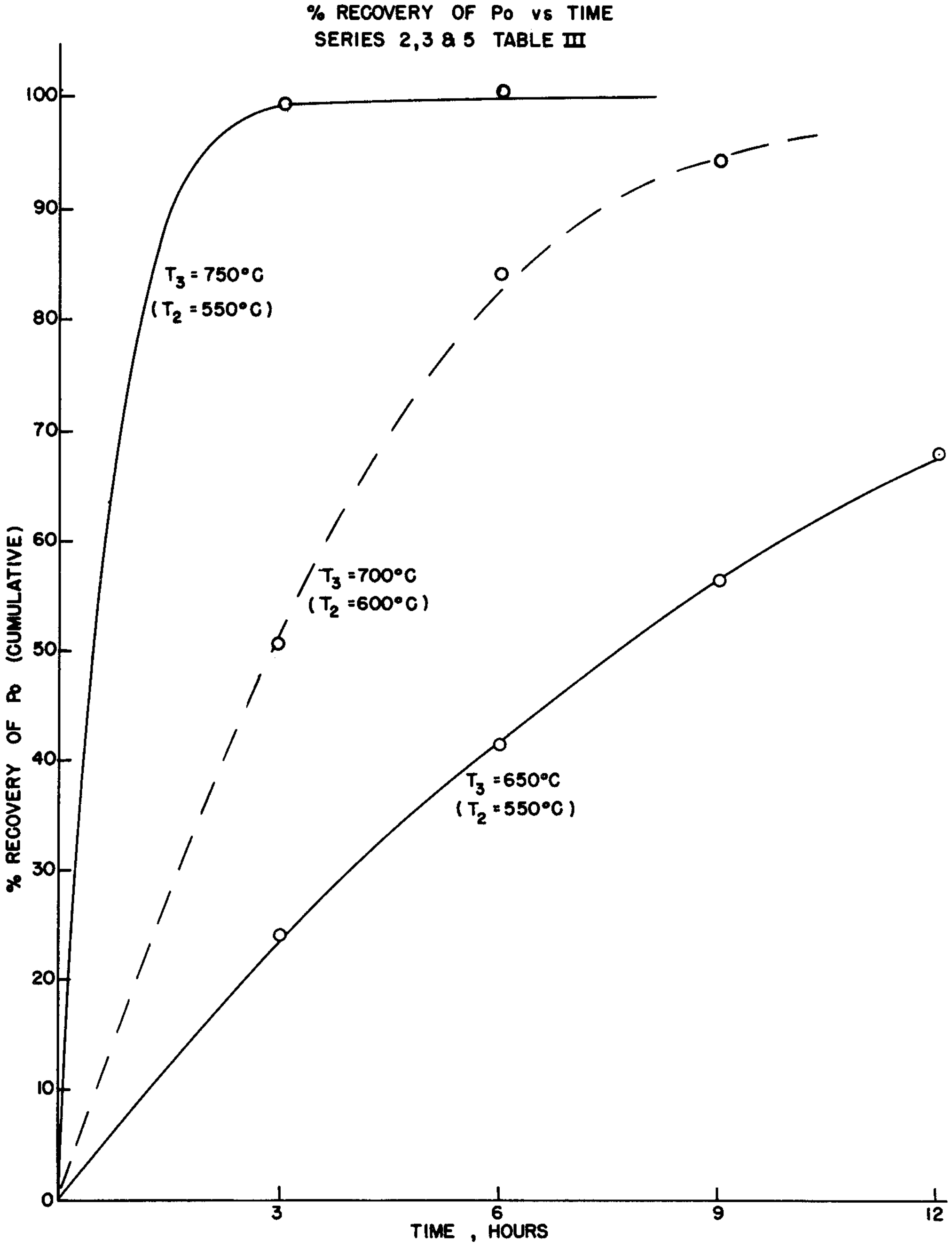
Tables V and VI list the operating data for this still. Temperatures were taken at the top of the column, T_1; at the middle of the column, T_2; at the middle of the still-pot, T_3; and at the bottom of the still-pot, T_4. For ease of operation, the middle of the column and the middle of the still pot defined the control conditions of temperature. Figure 6 shows the relationship between column temperature and the amount of both polonium and bismuth collected, with temperature of the still bottom held constant at optimum operating temperature. As would be expected the polonium curves approximate the form of an exponential curve while the bismuth curves are straight lines. Figure 7 shows the relationship between still-pot temperature and product recovery with the column temperature held approximately constant at optimum temperature. Within limits it was found that the column temperature controls product purity while the still-pot temperature controls distillation rate. Figure 8 is a graph of the limited data on the effect of bismuth depth on distillation rate expressed as per cent depletion of the charge. Because of the narrow range of depletions and depths covered by the data, this plot is considered to be a qualitative measure of the variation in depletion rate with changes in bismuth depth. The effect of depth might be better expressed in terms of the time required to reach a given degree of depletion, operating conditions being held constant at a still bottom temperature somewhat lower than optimum. Equipment now on hand should permit a more complete study of the depth effect.

Figure 9 shows approximately the relationship between product concentration and column temperature with the still-pot temperature held constant at 750°C and a distillation time of three hours for each point. A better illustration of the relationship would have been to plot product concentration versus column temperature for the same product recovery with a constant still-pot temperature. Extrapolation of the data as shown by the dotted curve of Figure 9 indicates that for these conditions considerable time would be sacrificed for a minor gain in product concentration by operating the column below 550°C.



EFFECT OF COLUMN TEMPERATURE ON PERFORMANCE OF LOW-CARBON STEEL SPARGING STILL

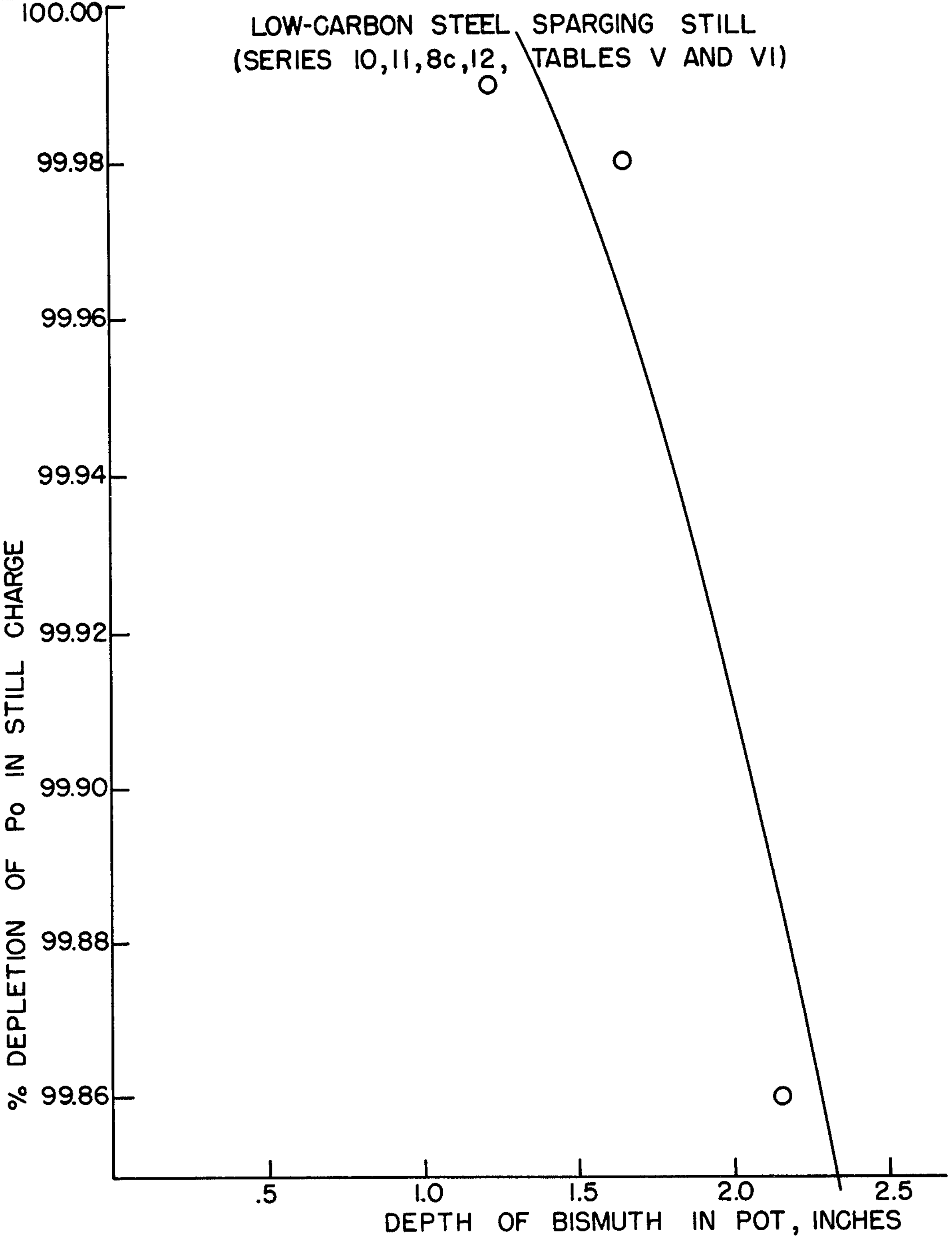
FIGURE 6



EFFECT OF STILL BOTTOM TEMPERATURE ON PERFORMANCE OF LOW-CARBON STEEL SPARGING STILL

5680

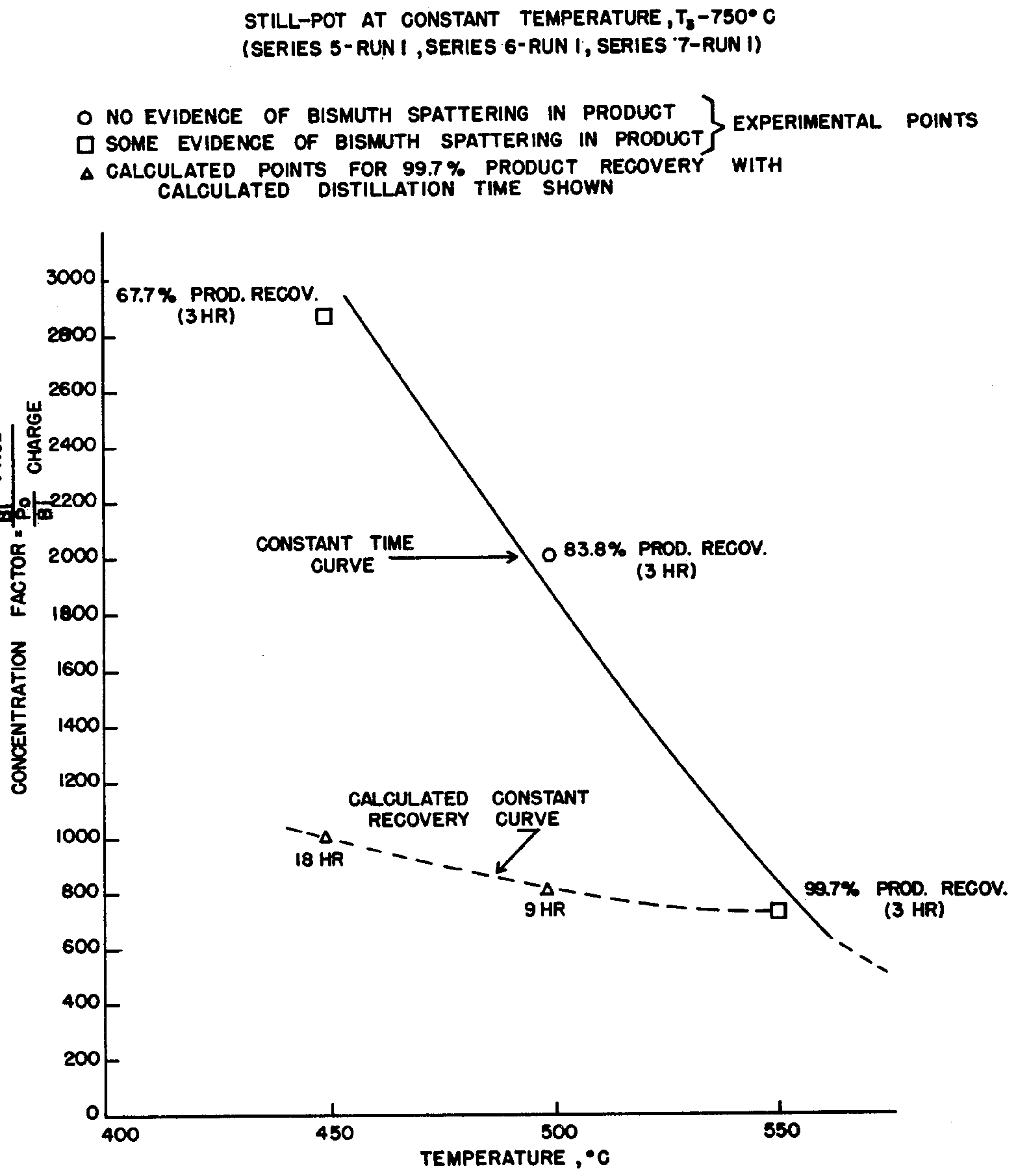
FIGURE 7



RATE OF DEPLETION OF CHARGE VS DEPTH OF MELT

5679

FIGURE 8



PRODUCT CONCENTRATION vs COLUMN TEMPERATURE, T_2

FIGURE 9

TABLE V

OBSERVED OPERATING DATA FROM LOW-CARBON STEEL SPARGING STILL

SERIES & RUN (*No*)	RUN TIME (*Hrs*)	T_1 COLUMN TOP (*C°*)	T_2 COLUMN CENTER (*C°*)	T_3 POT CENTER (*C°*)	T_4 POT BOTTOM (*C°*)	VACUUM PIRANI (*μ*)	VACUUM PHILLIPS (*μ*)	CHARGE Bi (*g*)	CHARGE Po (*C*)	PRODUCT Bi (*g*)	PRODUCT Po (*C*)	Po IN DISCHARGED Bi (*C*)
TEST	3	370	500	600	545	5-14	2.3-4	400	-	0.78	-	-
TEST	3	370	500	600	545	16-35	4-5	400		0.70	-	-
1-1	3	370	500	600	545	10-40	5-8	463.5	4.499	0.68	0.098	-
1-2	3	370	500	600	540	25-35	4-8	462.8	4.401	1.10	0.302	-
2-1	3	400	550	650	590	3-12	1-3	461.7	4.098	1.4	0.987	-
2-2	3	400	550	650	590	3-12	1-4	460.2	3.080	0.95	0.711	-
2-3	3	400	550	650	590	2-10	0.5-4	459.2	2.369	1.26	0.617	-
2-4	3	400	550	650	590	0.5	0.5	457.9	1.734	2.27	0.480	0.982
3-1	3	425	600	700	630	1.5-7	0.5-2	532.0	6.678	2.9	3.38	-
3-2	3	425	600	700	630	1.5-7	0.5-3	529.1	3.215	4.1	2.26	-
3-3	3	425	600	700	630	2-4	0.5-1	525.0	0.954	3.9	0.69	-
3-4	3	425	600	700	630	0.5-12	0.4-4	521.1	0.264	5.25	0.244	-
3-5	3	425	600	700	630	0.2-13	0.2-4	515.8	0.020	3.2	0.019	1.514×10^{-3}
4-1	3	430	600	650	590	2	0.7	493.4	5.993	5.59	1.62	-
4-2	3	430	600	650	590	3	0.6-.9	487.8	4.373	3.79	1.25	-
4-3	3	430	600	650	590	3	0.6-1	484.0	3.122	2.60	0.952	-
5-1	3	390	550	750	675	4	0.8-2	481.4	2.071	0.67	2.065	-
5-2	3	390	550	750	680	3	0.9-1.5	480.8	0.006	0.66	0.0275	SAMP. LOST
6-1	3	325	450	750	670	3	0.9-3	507.1	5.667	0.12	3.835	-
6-2	3	330	450	750	675	3	0.8	507.0	1.832	0.09	0.903	-
6-3	3	325	450	750	675	3	2	506.9	0.929	0.05	0.478	-
CLEAN UP	3	395	550	750	675	3	2	506.4	0.444	0.053	0.450	3.39×10^{-4}
7-1	3	360	500	750	675	4	2	478.9	4.990	0.20	4.180	-
7-2	3	360	500	750	675	14	6	478.7	0.810	1.5	0.690	-
7-3	3	360	500	750	675	4.5	3	477.2	0.121	1.0	0.105	-
8-1	3	395	550	750	675	2.5	1	672	7.308	1.8	7.145	-
8-2	3	395	550	750	680	5.5	3.5	670.2	0.163	1.6	0.161	2.1×10^{-3}
9-1	3	395	550	750	680	2.5	1	381.5	3.647	1.4	3.56	1.65×10^{-3}
10-1	3	395	550	750	675	3.5	1.5	687.8	6.917	1.5	6.737	9.66×10^{-3}
11-1	3	395	550	750	675	3	1.6	380.9	3.267	1.5	2.704	2.27×10^{-4}
12-1	3	395	550	750	675	2.3	3	520.2	4.808	1.16	4.65	1.17×10^{-3}
15-1	3	400	550	750	670	4.5	3.5	533.9	3.919	2.0	3.158	-
15-2	3	400	550	750	670	4	3	531.9	0.761	0.9	0.766	-
15-3	3	395	550	750	680	20	20	531.0	?	0.68	0.157	1.22×10^{-2}
16-1	3	390	550	740	670	2.7	0.35	520.7	3.220	1.0	3.45	3.702×10^{-2}
17-1	3	390	540	750	670	4.7	0.4	503.6	2.929	1.4	2.781	3.60×10^{-2}

SERIES 13, 14 AND 18 WERE NOT COMPLETED FOR VARIOUS REASONS

TABLE VI

CALCULATED OPERATING DATA-LOW-CARBON STEEL SPARGING STILL

SERIES AND RUN (No)	DEPLETION (%)	RECOVERY CYCLE (%)	RECOVERY CUMULATIVE (%)	CONCENTRATION FACTOR CYCLE	CONCENTRATION FACTOR CUMMULATIVE	REMARKS
TEST	-	-	-	-	-	NON-SPARGING COLD RUN
TEST	-	-	-	-	-	SPARGING COLD RUN
1-1	-	2.19	2.19	15	15	STILL LOADED WITH ACTIVE BISMUTH
1-2	-	6.86	8.89	29	23	
2-1	-	24.09	24.09	79	79	CHARGE CARRIED OVER FROM SERIES 1
2-2	-	23.08	41.44	112	81	
2-3	-	26.05	56.49	95	72	
2-4	OVERALL 78.17	27.68	68.00	56	54	STILL DISCHARGED
3-1	-	50.61	50.61	93	93	STILL LOADED
3-2	-	70.30	84.46	90	64	
3-3	-	72.33	94.79	97	46	
3-4	-	92.42	98.44	92	32	
3-5	OVERALL 99.97	95.00	98.73	153	27	STILL DISCHARGED
4-1		27.03	27.03	24	24	STILL LOADED
4-2	-	28.59	47.89	37	25	
4-3	-	30.49	48.09	57	26	
5-1		99.71	99.71	716	716	CHARGE CARRIED OVER FROM SERIES 4. EVIDENCE OF SPATTERING
5-2		458.33	101.04	338	365	STILL DISCHARGED
6-1	-	67.67	67.67	2860	2860	STILL LOADED. EVIDENCE OF SPATTERING
6-2	-	49.29	83.61	2777	2019	NO EVIDENCE OF SPATTERING
6-3	-	51.45	92.04	522	1795	
CLEAN UP	OVERALL 99.99+	-	OVERALL 99.98	9000	OVERALL 1723	STILL DISCHARGED
7-1	-	83.77	83.77	2006	2006	STILL LOADED. NO EVIDENCE OF SPATTERING
7-2	-	85.19	97.60	272	275	VAC LEAK. PRODUCT SPATTERED
7-3	-	86.78	99.70	414	176	STILL DISCHARGED. SPATTERING - POSSIBLE VAC LEAK
8-1	-	97.77	97.77	365	365	2.15'' Bi DEPTH. Bi IN ANNULUS
8-2	OVERALL 99.97	98.77	99.77	414	198	Fe IN DISCHARGED Bi = 0.0005%. Bi IN ANNULUS. STILL LOADED AND DISCHARGED ON EACH SUBSEQUENT RUN.
9-1	99.95	97.62	97.62	266	266	1.21'' DEPTH. VAC LEAK - SPATTERING. Bi IN ANNULUS
10-1	99.86	97.40	97.40	447	447	2.15'' Bi DEPTH. STILL DISCHARGED. Bi IN ANNULUS
11-1	99.99	82.77	82.77	210	210	1.21'' Bi DEPTH. SPATTERING PRODUCT PARTLY SPILLED. Bi IN ANNULUS
12-1	99.98	96.71	96.71	434	434	VAC GAUGE ERROR - VAC LEAK. Bi IN ANNULUS
15-1	-	80.58	80.58	215	215	COLUMN BAFFLE INSERTED AND REMAINED UNTIL THIS STILL WAS INOPERATIVE. SOME Bi IN ANNULUS. PRODUCT PARTLY SPILLED
15-2	-	100.66	100.13	595	184	SOME Bi ANNULUS
15-3	OVERALL 99.69	?	104.13	?	155	VAC LEAK. SOME Bi IN ANNULUS
16-1	99.16	107.14	107.14	558	558	NO SPARGING
17-1	98.77	94.95	94.95	342	342	VAC LEAK. NO SPARGING

SERIES 13, 14 AND 18 WERE NOT COMPLETED FOR VARIOUS REASONS

A baffle was inserted in the bottom of the still column in an attempt to eliminate bismuth spattering during still operation. Although the baffle constricted the column to less than one-eighth of its cross-sectional area distillation rates and yields appeared to be unaffected. The still failed before a complete study could be made of the effect of reduced column cross-sectional area.

The series marked 16 and 17 in Tables V and VI were run without sparging. Although the pressure readings indicate that a reasonably good vacuum was obtained there is a possibility that a small leak occurred through the sparging arm. These data indicate that the lack of sparging had little effect upon rate of distillation and create some doubt as to reliability of earlier sparging tests. A positive comparison of sparging and non-sparging will be made with new equipment now on hand.

Examination of Tables V and VI indicate erratic concentration values. These variations probably were caused either by bismuth being spattered to the condenser or by adhering to the condenser of some previously-spattered bismuth in the annulus. Improved still design should alleviate if not eliminate this condition.

SILICON STEEL SPARGING STILL

Battelle Memorial Institute tested a large number of materials for use in the construction of bismuth stills. The most promising of the alloys tested was 3 per cent silicon steel, commonly called transformer steel. Battelle reported that silicon steel was not wetted by bismuth in the range of anticipated still temperatures, and that the corrosion rate caused by bismuth was exceedingly low. A distillation unit was constructed of this alloy from the design drawings of the low carbon steel unit in order to evaluate this material under actual operating conditions.

Comparing the data shown in Tables VII and VIII for the silicon steel unit with that shown in Tables V and VI for the low-carbon steel still, a lesser rate of heat transfer from the still walls to the bismuth is indicated for the silicon steel unit. Although higher product concentrations were obtained, lower product recoveries were found. However, still-bottom depletions were about the same as for the low-carbon steel still. In order to approach the results obtained with the low-carbon steel unit, higher still wall temperatures were required. Since the creep-strength for transformer steel and low-carbon steel are in the same range, design considerations would require a thicker still wall if transformer steel alone were used for the body of a large still. Of greater concern were the low and erratic product yields which indicated possible interaction between polonium and transformer steel.

TABLE VII

OBSERVED OPERATING DATA

SILICON STEEL SPARGING STILL

SERIES AND RUN	RUN TIME	TEMPERATURE				VACUUM		CHARGE		PRODUCT		Po IN DISCHARGED Bi
		T_1 COLUMN TOP	T_2 COLUMN CENTER	T_3 POT CENTER	T_4 POT BOTTOM	PIRANI	PHILLIPS	Bi	Po	Bi	Po	
(No)	*(hrs)*	*(C°)*	*(C°)*	*(C°)*	*(C°)*	*(μ)*	*(μ)*	*(g)*	*(C)*	*(g)*	*(C)*	*(C)*
1-1	3	360	550	750	690	4-25	3-25	472.0	2.334	0.17	2.15	3.89×10^{-2}
2-1	3	390	600	750	680	11	4	503.4	8.930	0.49	7.94	5.686×10^{-2}
3-1	3	390	600	775	710	12	4	516.1	8.919	0.75	8.729	5.40×10^{-3}
4-1	4	380	590	770	700	12	4	507.5	8.620	0.50	8.234	2.892×10^{-3}
5-1	3	380	575	775	705	11	3	514.2	8.495	0.885	7.754	3.033×10^{-2}
6-1	3	405	600	775	695	13	4	521.6	7.974	0.665	7.258	7.75×10^{-3}
7-1	3	410	625	800	705	10	4	518.7	7.743	1.03	7.558	1.31×10^{-2}
8-1	3	415	650	820	735	8.5	3.5	513.6	7.463	2.8	6.822	2.69×10^{-2}
9-1	3	410	620	820	735	9.8	4	532.9	7.604	2.1	7.069	0.149
10-1	3	410	625	825	740	9	3	537.0	10.245	3.6	9.921	3.87×10^{-2}
11-1	5	405	625	825	740	10.5	3.5	547.7	10.356	1.8	10.02	6.415×10^{-3}
12-1	3	405	625	825	735	12	4	550.2	9.563	0.75	9.028	2.439×10^{-2}
13-1	3	400	625	825	740	6	3	561.1	9.348	2.00	8.37	3.729×10^{-2}
14-1	3	400	625	825	740	6	3	599.8	10.549	1.00	10.114	2.643×10^{-2}

THE STILL WAS LOADED AND DISCHARGED FOR EACH RUN

TABLE VIII

CALCULATED OPERATING DATA

SILICON STEEL SPARGING STILL

SERIES AND RUN (No)	DEPLETION (%)	RECOVERY (%)	CONCENTRATION FACTOR	REMARKS
1-1	98.33	92.12	2558	VAC LEAK
2-1	99.36	88.91	914	
3-1	99.93	97.87	674	
4-1	99.96	95.52	970	
5-1	99.64	91.28	530	
6-1	99.90	91.02	714	
7-1	99.83	97.62	492	
8-1	99.63	91.41	168	
9-1	98.04	92.96	236	
10-1	99.62	96.84	145	Bi IN ANNULUS
11-1	99.94	96.76	294	Bi IN ANNULUS
12-1	99.75	94.41	693	Bi IN ANNULUS
13-1	99.60	89.54	251	VAC LEAK - SPILLED PROD Si STEEL TEST ROD
14-1	99.75	95.88	575	LOW CARBON TEST ROD

POLONIUM ABSORPTION ON SILICON STEEL

In order to establish the effect of transformer steel on polonium, rods of transformer steel and SAE 1020 steel were used in qualitative penetration tests. Each rod was placed inside the silicon steel still so that one end was submerged in the melt and the other end extended midway into the column. The still charges were of the same magnitude, and the runs were made under the same operating conditions, series 13 and 14 of Tables VII and VIII.

After the runs were completed, an attempt was made to decontaminate the rods by identical procedures. Comparisons of contamination on the rods during the decontamination process were made with a counting-rate monitor. Counting was done over the most active 1.5 inches of each rod.

The first step consisted of scraping off the bismuth adhering to the rod, and then removing 0.001 inches of the base metal with coarse emery cloth followed by metal polish. The second step consisted of removing another 0.001 inch of base metal with emery cloth and metal polish. Steps three through six consisted of polishing with metal polish. The sixth step included a wash in dilute hydrochloric acid, dilute bleach, and soap solution. At the conclusion of the test both rods were heated by means of an induction heater to approximately 900°C under vacuum for 3 minutes. The results of the tests are shown in Table IX. The data indicate that roughly ten times more activity was absorbed in the silicon steel rod than in the SAE 1020 steel rod under like conditions.

TABLE IX

COMPARATIVE DECONTAMINATION OF SILICON STEEL AND SAE 1020 STEEL

STEP *(No)*	3% SILICON TRANSFORMER STEEL *(cts/min)*	SAE 1020 STEEL *(cts/min)*	REMARKS
1	2.3×10^6	2.25×10^5	0.001 IN. METAL REMOVED
2	14,950	1,600	0.001 IN. METAL REMOVED
3	20,700	2,800	METAL POLISH
4	23,000	1,760	METAL POLISH
5	24,100	1,760	METAL POLISH AND WASH
6	28,750	2,400	METAL POLISH AND FLASH
AFTER HEATING	23	23	

SIMPLE DISTILLATION EXPERIMENTAL WORK

The fractionating or partial condensation stills described in the preceeding sections use columns to increase the concentration of the product over that obtainable by simple distillation. In general, the terms "simple equilibrium" and "differential distillation" have been employed practically synonymously in reports on this work. Due to the possible simplification of equipment and probability that results could be more easily predicted from uninvolved tests, simple distillation was investigated as a possible means of separating polonium from irradiated bismuth. After the fractionating work achieved the excellent results shown in Tables V and VI, the simple distillation work was discontinued although related fundamental research has continued to a certain extent.

RELATIVE VOLATILITIES AND DISTILLATION RATES

Fundamental experiments on the relative volatility α, also referred to as the enrichment factor K, of polonium from polonium-bismuth mixtures have been performed by R. W. Moshier and E. F. Joy of the Chemistry Section,[6,7,8,9,10] This work includes data on the vapor pressure of bismuth and its rate of evaporation. The best values available for these quantities, based on the preceding references and some unpublished data by Joy, are as follows:

Relative Volatility, (unrestricted)

$$\alpha = -4.9828 + \frac{18219}{T + 1728}$$

Relative Volatility, (restricted or equilibrium)

$$\alpha = -3.0073 + \frac{10348}{T + 1150}$$

Data for computing the second equation was obtained with orifices between the distilling mixture and the condenser to reduce the rate of distillation. It should represent equilibrium conditions since the amount of restriction appeared to be immaterial when the orifices were varied from about 0.1 per cent to 5 per cent of the area of the distilling bismuth.

Distillation rate of bismuth (low pressure)

$$\log w = 8.3878 - \frac{10051}{T} - \frac{1}{2}\log T$$

Vapor pressure of pure bismuth,

$$\log P = -\frac{10051}{T} + 8.462$$

Vapor pressure of pure polonium,

$$\log P = -\frac{5378}{T} + 7.2345$$

The last equation is taken from the work of Brooks.[11] The temperature limits of all five of the above equations are from 450° to 850°C.

In the above equations,

$$\alpha = \frac{\log \frac{(Po)\ initial}{(Po)\ final}}{\log \frac{(Bi)\ initial}{(Bi)\ final}}$$

T = degrees Kelvin

w = grams per square centimeter per second

P = millimeters of mercury

SIMPLE DISTILLATION PROPOSALS

Based on some of these results, calculations were made to show the feasibility of the simple distillation process.[12] As an example of the results of these calculations, a two-still simple distillation system could give a product 100 times more concentrated than the feed while recovering 99.5 per cent of the polonium.

The simple distillation of polonium from bismuth by flashing was considered.[13] This approach did not appear to be promising unless very fine subdivision of the molten bismuth could be obtained. An information report on simple batch distillation was prepared at this time.[14] It suggests a falling-film type of molecular distillation as a method of separation which should be investigated.

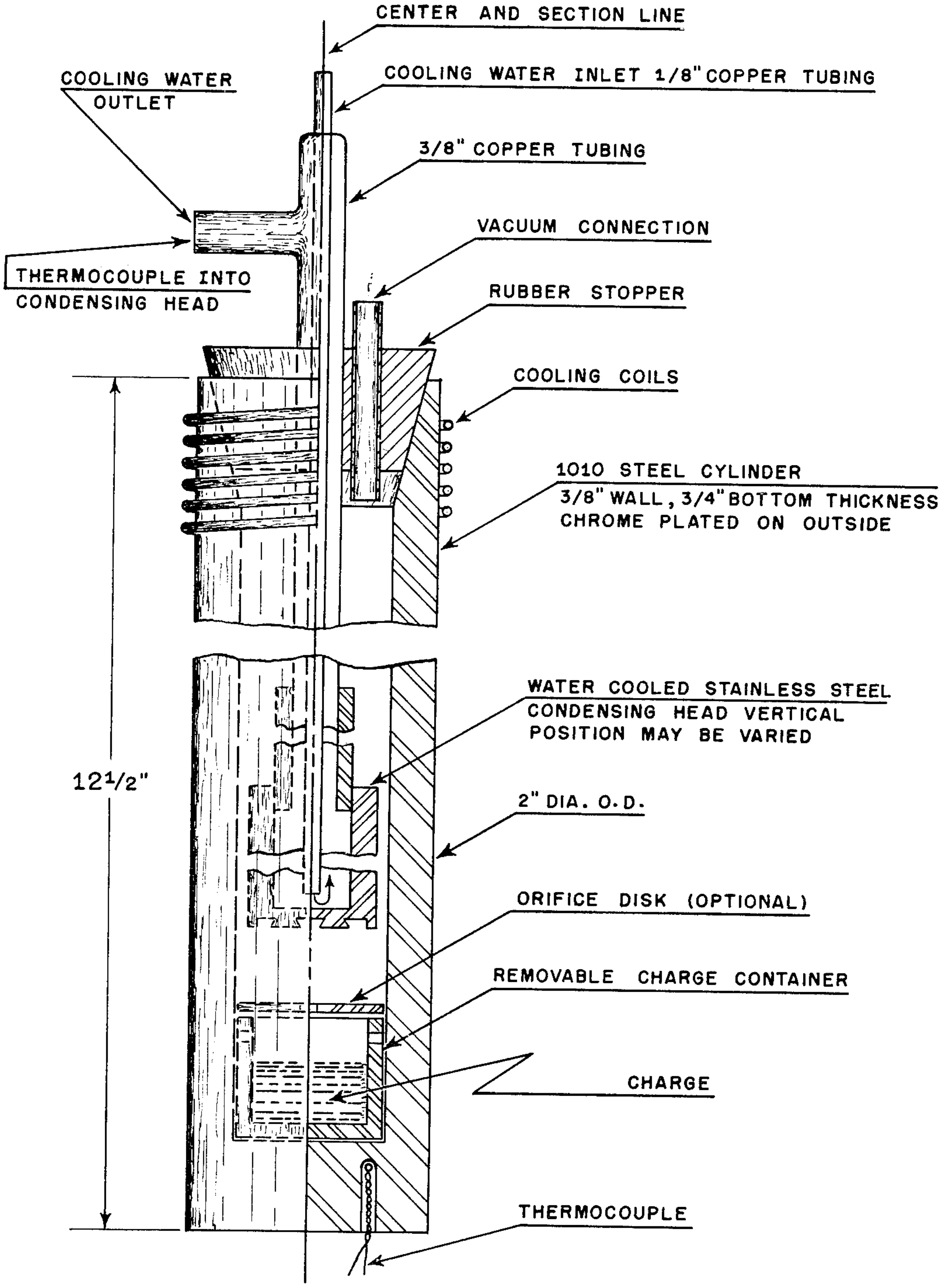
EXPERIMENTAL RESULTS

Determinations of relative volatility and evaporation rate were made by the Chemical Engineering Section employing equipment from simple distillation applications.[4,15] An example of the type of equipment used in these tests is shown in Figure 10.

Table X lists the results obtained in early experiments. The observed increase in the amount of bismuth distilled when the condenser spacing was increased may be due to an unobserved increase in the surface temperature of the melt due to a reduction in radiant heat loss. Table XI shows data from a run in which the individual cycles were operated at different temperatures. Table XII gives the results of a depletion run with an unrestricted vapor stream while the data in Table XIII were obtained with a 0.063-inch diameter orifice just above the distilling bismuth. The corrected relative volatilities shown in Table XII have been adjusted to account for the amount of depletion found at the end of the run instead of being calculated from the amount of polonium collected.

Table XIV presents the results of an experiment performed to test two-stage simple distillation. These results, compared to previous calculations,[12] indicate that better depletions and product concentrations would be obtained in operation but that greater distilling areas than those calculated would be needed.

Because of the low rate of bismuth vaporization experienced in most of the tests described above compared to that calculated from vapor pressure[9] data, an investigation was made of factors which may have produced this result. These factors include: (1), contamination of the distilling surface by an oxide film or a film of other impurities originating either in the bismuth charge or from the container material; and (2), a possible difference in temperature between the distilling surface and that measured in the body of the molten bismuth.



STEEL TEST STILL.

FIGURE 10

TABLE X

CONSTANT-TEMPERATURE BISMUTH-POLONIUM DIFFERENTIAL-DISTILLATION TESTS

RUN	DISTANCE MELT-CONDENSER (*in*)	TEMP (*C°*)	PRESSURE (*μ*)	TIME (*hr*)	Po CHARGE (*C*)	Po COLLECTED (*%*)	Bi CHARGE (*g*)	Bi COLLECTED (*%*)	BISMUTH RATE (*lbs/in²/hr*)	α^1	CONC FACTOR^2
1	1	745	0.026 - 0.05	1			97.68	1.25	0.00184		
2	1	745	0.028 - 0.05	1			96.82	1.26	0.00184		
3	1	745	0.025 - 0.50	1			100^3	1.35	0.00204		
4	1	745	0.045 - 0.40	1			100	1.37	0.00207		
5	4	745	0.046 - 0.1	1			100	2.32	0.00350		
6	4	745	0.042 - 0.42	1			100^3	3.18	0.00480		
7	4	745	0.025 - 0.06	1			98.65	3.53	0.00526		
8	4	745	0.071 - 0.11	1			98.63	2.75	0.00411		
9	1	750	5.0	1	0.569	27.1	118.9^3	0.41	0.00073	76.5	65.5
10	1	750	5.0 - 5.3	1	0.410	35.3	85.6	0.62	0.00080	70.5	57.0
11	1	750	5.0	4	0.413	79.2	86.4	1.74	0.00056	90.0	45.6
12	1	745	5.1	4	0.404	86.5	84.4^3	2.40	0.00076	81.9	35.8

(1) $\alpha = \dfrac{\log \dfrac{\text{Po INIT.}}{\text{Po FINAL}}}{\log \dfrac{\text{Bi INIT.}}{\text{Bi FINAL}}}$ = RELATIVE VOLATILITY

(2) $\text{CF} = \dfrac{\left(\dfrac{\text{Bi}}{\text{Po}}\right)_{\text{INIT.}}}{\left(\dfrac{\text{Bi}}{\text{Po}}\right)_{\text{COLLECTED}}}$ = CONCENTRATION FACTOR

(3) NEW BISMUTH USED IN RUNS 3 THROUGH 6 AND 9 THROUGH 12 INC.

TABLE XI

VARIABLE TEMPERATURE BISMUTH-POLONIUM DIFFERENTIAL-DISTILLATION TESTS

RUN	DISTANCE MELT-CONDENSER (*in*)	TEMP (C^{o})	PRESSURE (μ)	TIME (*hr*)	Po COLLECTED (*C*)	Po CUM. (%)	Bi COLLECTED (*g*)	Bi CUM. (%)	BISMUTH RATE ($lb/in^2/hr$)	α *per cycle*	CONC. FACTOR *per cycle*
CYCLE 1	1	630	4.3	$\frac{1}{2}$	0.0875	17.45	0.062	0.057	0.00031	333	306
CYCLE 2	1	670	4.5	$\frac{1}{2}$	0.2262	62.60	0.535	0.550	0.00265	162	111
CYCLE 3	1	710	4.2	$\frac{1}{2}$	0.1692	96.40	4.8	4.96	0.02380	50.5	20.3
CYCLE 4	1	750	4.2	$\frac{1}{2}$	0.01825	99.88	18.5	22.0	0.09176	18	5.4

CHARGE 108.8 G BISMUTH 0.5017 C POLONIUM

TABLE XII

DATA FOR DIFFERENTIAL DISTILLATION AT 750°C WITH UNRESTRICTED VAPOR STREAM

RUN	PRESS. (μ)	TIME CUM. (*hrs*)	Po DIST. CYC. (%)	Po DIST. CUM. (%)	Bi DIST. CYC. (%)	Bi DIST. CUM. (%)	RATE Bi DIST. ($lbs/in^2/hr$)	α CYC.	α CUM.	CUM. α CORR.	CONC. FACTOR CYC.	CONC. FACTOR CUM.
1A	25	2	79	79	2.14	2.14	0.0026	66	66	74.5	37	37
1B	1	5	37	87	0.59	2.71	0.0005	66	66	77	63	32
1C	1	7	48	95.5	1.6	4.27	0.0019	40	56.5	75	30	22
1D	1	12	98	99.9	5.8	9.7	0.0027	8.9	29	60	17	10

TABLE XIII

DATA FOR DIFFERENTIAL DISTILLATION AT 750°C WITH RESTRICTED VAPOR STREAM

RUN	PRESS (μ)	TIME CUM. (*hrs*)	Po CYC. (%)	Po CUM. (%)	Bi CYC. (%)	Bi CUM. (%)	RATE Bi DIST. (*lbs/in^2/hr*)	α CYC.	α CUM.	CONC. FACTOR CYC.	CONC. FACTOR CUM.
2A	8	2	1.3	1.3	0.06	0.06	6.7×10^{-5}	34	34	22	22
2B	15	5	2.3	3.6	0.016	0.08	1×10^{-5}	175	47	142	48
2C*	1	8	7.2		6.7		5×10^{-2}	18		10.7	
2D	1	12	0.75		0.04		2.2×10^{-5}	19		19	

*THIS PORTION OF THE RUN WAS OPERATED AT SOME TEMPERATURE OVER 900°C BECAUSE OF A THERMOCOUPLE FAILURE

TABLE XIV

TWO-STAGE SIMPLE DIFFERENTIAL DISTILLATION

TEMPERATURE - 750°C

PRESSURE - 1 TO 10 MICRONS

RUN	TIME (*hr*)	RELATIVE VOLATILITY CYC.	RELATIVE VOLATILITY CUM.	CONCENTRATION FACTOR CYC.	CONCENTRATION FACTOR CUM.	Po DISTILLED CYC. (%)	Po DISTILLED CUM. (%)	Bi DISTILLED CYC. (%)	Bi DISTILLED CUM. (%)	Bi RATE (*lb/in^2/hr*)	Bi RATE (*% of calc*)
4A	7	53	53	6.6	6.6	99.99	99.99	15.2	15.2	0.0057	12.1
4B$_1$	0.16	66	66	38.3	38.3	69.0	69.0	1.8	1.8	0.0043	9.1
4B$_2$	0.25	49	57.7	35	26	54.3	86.0	1.55	3.32	0.0024	5.0
4B$_3$	0.42	46.4	52	28.5	16.2	81.0	97.3	2.84	6.0	0.0026	5.5

NOTES - RUN 4A IS FIRST STAGE OF DISTILLATION AND RUNS 4B$_1$, 4B$_2$, AND 4B$_3$ ARE SUCCESSIVE PORTIONS OF THE SECOND-STAGE DISTILLATION.

THIS TWO-STAGE DISTILLATION THEREFORE DIVIDED THE ORIGINAL FEED INTO THREE PORTIONS AS FOLLOWS:

		% OF ORIG. Bi	% OF ORIG. Po	(Po/Bi) FINAL/(Po/Bi) INITIAL
I	DEPLETED BISMUTH	84.8	0.01	0.0118
II	PRODUCT	0.91	97.3	107
III	MIXTURE TO BE RECYCLED	14.3	2.7	0.19

Table XV lists the rates of bismuth distillation under various conditions of charge preparation and from distilling-cups of different materials. It was concluded: (1), that it is important to use large pieces of bismuth in the charge in order to avoid surface oxidation; (2), that filtering of the charge is not necessary; and (3), that if stainless steel is employed as a cup material it should be pre-heated to clean the surface. While most of the data shown in this table were obtained with inactive bismuth, irradiated bismuth was employed in runs marked 9 and 10. It was found that the relative volatility observed during these runs was the same as that observed at this temperature in previous work where a much lower rate of bismuth distillation was obtained. This indicates that the higher rate of bismuth distillation was accompanied by a similarly increased rate of polonium vaporization.

TABLE XV

TESTS OF RATE OF DISTILLATION OF BISMUTH AT 750°C AND 1 TO 10 MICRONS PRESSURE

RUN	TIME *(hr)*	CUP MATERIAL	Bi CHARGE *(g)*	Bi RATE *($lb/in^2/hr$)*	PER CENT OF CALCULATED	CONDITION OF CHARGE
1	4.67	STAINLESS STEEL	68	0.0023	4.8	FILTERED, MILLED CHARGE
2	4.25	L. C. STEEL	73	0.0038	8.0	FILTERED, MILLED CHARGE
3	4.0	STAINLESS STEEL	139	0.00037	0.8	REFILTERED, MILLED CHARGE
4	6.0	QUARTZ	56	NEG		REFILTERED, MILLED CHARGE
5	2.0	QUARTZ	30	0.019	41.5	UNFILTERED, LARGE CHUNKS
6	1.75	STAINLESS STEEL	44	0.01	21.7	UNFILTERED, LARGE CHUNKS
7	2.0	QUARTZ	28	0.02	45.0	FILTERED, LARGE CHUNKS
8	2.0	STAINLESS STEEL	25	0.011	23.6	FILTERED, LARGE CHUNKS
9	1.33	STAINLESS STEEL	84	0.017	37.0	UNFILTERED, PREHEATED CUP
10	0.25	STAINLESS STEEL	39	0.013	27.0	UNFILTERED, PREHEATED CUP

Determinations were made of the temperature difference between the distilling surface and the body of the bismuth melt by calculation and by direct measurement. While not of a high order of precision these results indicated that the temperature of the distilling surface was at most 15°C below that measured in the body of the melt. This difference is not sufficiently large to have been a major factor in producing the low vaporization rates of the previous experiments.

INVESTIGATION OF MATERIALS OF STILL CONSTRUCTION

One of the major problems facing this project has been locating or developing a satisfactory material for construction of bismuth stills. The ideal material for the construction of stills for bismuth-polonium mixtures should have at least the following characteristics:

(1) It should be capable of containing bismuth up to 850°C or higher under reduced pressure without adding impurities to the bismuth and without being attacked by the bismuth.

(2) It should be capable of containing polonium under the above conditions without absorbing or combining with small quantities of polonium.

(3) It should be strong at high temperatures, readily available, and capable of being fabricated easily into vacuum-tight vessels.

(4) It should have a low vapor pressure at high temperatures.

(5) It should not be oxidized by air at 900°C.

Other desirable characteristics depending upon conditions include immunity to the effect of rapid temperature changes, non-magnetic properties if magnetic agitation of the still contents is employed, and resistance to nitric acid to permit of leaching periodically.

CORROSION BY LIQUID BISMUTH

The corrosion of metals and other materials by molten bismuth has been investigated fairly extensively by others. A full treatment of the work at other sites is beyond the scope of this report and the reader is referred to Reference 16 for a review of the subject. Additional information has been published[17,18] recently.

At our request Battelle Memorial Institute tested a number of materials for corrosion by bismuth under specified conditions in order to make the data applicable to the distillation project. Their work[19] covered static corrosion of about 50 materials by liquid bismuth at 750°C and 850°C. These materials included low-alloy steels, silicon steels, stainless steels and super heat-resistant alloys. The metals were examined visually and metallographically after exposure to the bismuth and the bismuth was analyzed for impurities absorbed from the alloy. In fairly long-term tests Armco iron, low-carbon steels and chromium-plated samples were found to be severely attacked while the chromium alloys, stainless steels and super-alloy steels were moderately attacked. A 2.9 per cent silicon transformer steel and Duriron were the only materials tested which exhibited good corrosion-resistance to bismuth at 750°C and 850°C.

At Mound Laboratory corrosion tests of bismuth on various materials have been made over a period of time. Many of the experiments listed below were performed before portions of the reference material described above became available.

R. W. Moshier of the Chemistry Section reported some early corrosion experiments.[20, 21] Table XVI lists these data for the corrosion of low-carbon steel by bismuth. The first eight tests were performed by refluxing bismuth in a steel cylinder in a residual nitrogen atmosphere of about one millimeter of mercury pressure. A "condensation ring" containing a brittle deposit was found in all cases on the tube wall just above the heated zone. Although the deposit appeared to be an alloy, bismuth flowed out upon heating a portion of it to 1000°C, leaving a residue of the same form as the original piece. This residue is thought to be a spongy deposit of condensed iron containing absorbed bismuth.

TABLE XVI

CORROSION OF LOW-CARBON STEEL BY MOLTEN BISMUTH

TEST NO.	BISMUTH CHARGED *(g)*	TEMPERATURE *(°C)*	VACUUM *(mm Hg)*	DURATION OF TEST *(hr)*	BISMUTH RECOVERED *(g)*	IRON IN BISMUTH *(%)*	IRON IN CONDENSATION RING *(%)*
1	100	980	1	24	81	0.005	-
2	100	980	1	24	93	0.005	28
3	100	850	1	48	73.7	0.006	-
4	100	850	1	48	78.0	0.003	15.5
5	100	850	1	78	78.0	0.05	-
6	100	850	1	78	TUBE FAILED WHEN WELD OPENED		30
7	100	850	0.7	100	80.0	0.2	-
8	100	850	0.7	100	85.8	0.24	26**
9*	100	850	0.7	100	97	0.08	0.04

*IN QUARTZ TUBE WITH PIECE OF STEEL OF AREA OF 3.34 SQUARE CENTIMETERS.

**WEIGHT OF CONDENSATION RING, 17.5 GRAMS.

Table XVII contains the results of tests on miscellaneous metals made by exposing the sample to bismuth contained in a quartz tube. This work was the first indication that silicon had a beneficial effect on the corrosion resistance of iron alloys by bismuth. Table XVIII lists data obtained on the corrosion-resistance of high-temperature alloys. These tests indicate that alloys S-590 and 19-9DL have fairly good resistance to corrosion.

Tests were performed by the Chemical Engineering Section[5, 22] in order to specify materials for experimental still construction. Two tests on SAE 1020 steel tubes containing bismuth for 100 hours at 900°C and one micron pressure gave 0.3 per cent and 0.1 per cent of iron in the discharged bismuth.[22] A similar test on a high-chromium steel (18% Cr. 0.65% Mo) resulted in bismuth containing 2.4 per cent of chromium.

TABLE XVII

CORROSION TESTS ON MISCELLANEOUS METALS*

TEST METAL	TEMPERATURE (°C)	VACUUM (*microns*)	TIME (*hr*)	RESULTS
TANTALUM	850	50	100	THE 1-INCH SQUARE SHEET OF 6-MIL Ta LOST 51.5 MG. THE IMMERSED PORTION WAS VERY BRITTLE.
ALINCO	850	50	24	DURING THE TEST NEEDLES APPEARED ON THE BISMUTH SURFACE AND SOLIDIFIED. A 35° INCREASE IN TEMPERATURE PERMITTED CONTINUATION. Ni, Fe, Cu, Co WERE PRESENT IN THE BISMUTH.
MOLYBDENUM	900	50	190	ALL THE BISMUTH HAD CONDENSED IN THE COOL PART OF THE CHAMBER AT THE END OF THE TEST. A SPECTROGRAPHIC TRACE OF MOLYBDENUM WAS PRESENT IN THE BISMUTH. THE IMMERSED PART OF THE MOLYBDENUM WIRE WAS BRITTLE.
DURIRON (TEST 1)	850	50	72	0.002 PER CENT IRON WAS FOUND IN THE BISMUTH POOL, AND 0.001 MG IN THE BISMUTH MIRROR ON THE WALLS OF THE CONTAINER.
(TEST 2)	850	50	100	A TRACE OF IRON AND OF MOLYBDENUM WAS PRESENT IN THE BISMUTH. THE 25 G TEST PIECE LOST 21.5 MG.

*100 G OF BISMUTH WAS CHARGED IN EACH TEST.

A series of short-time screening tests on 14 alloys[5] were performed in quartz tubes with bismuth heated by induction heaters. The alloy composition, final bismuth composition and the sample weight-loss are listed in Table XIX. The three samples considered worthy of further investigation were the super-alloys 19-9DL, S-590 and Haynes Stellite 25. The results of further checks on these materials are given in Table XVIII.

TABLE XVIII

CORROSION TESTS ON HIGH-TEMPERATURE ALLOYS

ALLOY DESIGNATION	WEIGHT			CORROSION RATE	APPEARANCE	
	BEFORE (g)	AFTER (g)	CHANGE (g)	(g/in²/100 hr)	AFTER TEST	TEMP (°C)
HAYNES STELLITE NO. 25	8.7785	8.6225	0.1560 LOSS	0.0678	ETCHED	880
S-590	9.3925	9.3947	0.0022 GAIN	(0.907 IN² AREA)	CORNERS ALLOYED	875
19-9-DL	8.8000	8.7370	0.0630 LOSS	0.0532	NO CHANGE	890

ANALYSIS OF THE BISMUTH

	Fe (%)	Ni (%)	Co (%)	Si (%)	Mn (%)	Cr (%)	Mo (%)	W (%)	Nb (%)	Ag (%)	Al (%)	Mg (%)	Pb (%)	Ti (%)
HAYNES STELLITE NO. 25														
SPECTRO	NOT TAKEN	NOT TAKEN	NOT TAKEN											
CHEM	TRACE	0.05	0.06			0.04								
S-590														
SPECTRO	WEAK	WEAK	WEAK	TRACE	TRACE	TRACE	TRACE	NONE	NONE	TRACE	TRACE	TRACE	TRACE	
CHEM	0.03	0.016				0.015								
19-9-DL														
SPECTRO	TRACE	TRACE		WEAK				NONE	NONE				TRACE	NONE
CHEM	NONE	NONE		0.007	NONE	NONE	NONE							

CHARGE - 100 G BISMUTH

PRESSURE - 12μ

TABLE XIX

MATERIAL OF CONSTRUCTION TESTS*

SAMPLE ASM CODE	SAMPLE COMPOSITION, PER CENT (PUBLISHED)											FINAL Bi COMPOSITION, PER CENT								SAMPLE WT.	PRES.	TIME	TEMP.	SAMPLE WT LOSS
	C	Mn	Si	Cr	Ni	Co	Mo	Cb	Ti	W	Fe	C	Mn	Si	Cr	Ni	Co	Mo	Fe	(g)	(μ)	(*Min*)	(°C)	(g)
HAYNES STELLITE 25	**	-	-	**	**	**	-	-	-	**	**	-	-	-	0	0	-	-	0	9.8431	<1	30	960	0.0026 (GAIN)
HAYNES STELLITE S-816	0.35-0.45	1.0	1.0	18.5-20.5	19-21	42-44	3.5-4	3.5-4	-	3.5-4	REM.	-	0.02	-	0.045	0.16	0.06	-	0.04	6.9670	1.0	35	1,000	0.5830
SUPER ALLOY S-590	0.4-0.5	2.0	1.0	18.5-20.5	19-21	19-21	3.5-4	3.5-4	-	3.5-4	REM	-	TRACE	0	0	TRACE	0.001	-	0	9.7126	1.0	35	840	0.0174
SUPER ALLOY 19-9 DL	0.25	0.5	0.60	19	9	-	1.25	0.3	0.2	1.2	REM	-	0	0	0	0	-	0	TRACE	6.3391	1.5	45	900	0.0037
VITALLIUM	0.22	0.66	0.53	27.4	2.8	62.2	5.5	-	-	-	0.70	0	0.11	0	0.054	0	0.05	0	0.10	4.0553	<1	37	980	0.3631
HASTALLOY B	0.05	0.59	0.19	-	65	-	28.6	-	-	-	4.7	-	0.063	0	0.01	0.135	-	0	0.33	9.6620	<1	60	950	
STAINLESS STEEL-304	0.08	2.0	-	18-20	8-11	-	-	-	-	-	REM.	0	0.05	-	0.02	0.014	-	-	1.4	12.2201	<1	60	950	0.1473
STAINLESS STEEL-347	0.08	-	-	17-19	9-12	-	-	0.8	-	-	REM.	0	0.04	-	0.09	0.077	-	-	7.5	12.0450	<1	60	960	0.6072
STAINLESS STEEL-316	0.10	-	-	16-18	10-14	-	2-3	-	-	-	REM.	0	0.05	-	0.13	0.074	-	0	0.70	5.2381	<1	60	950	-
STAINLESS STEEL-314	0.10	-	-	25	20	-	-	-	-	-	REM.	-	-	-	0.009	0.06	-	-	0.10	12.6036	<1	60	925	0.1956
STAINLESS STEEL-446	0.35	-	-	23-27	-	-	-	-	-	-	REM.	-	-	-	0.001	-	-	-	0.08	7.0940	<1	30	900	0.0145
STAINLESS STEEL-321	0.08	-	-	17-18	8-11	-	-	-	0.4	-	REM.	-	-	-	0.009	0.02	-	-	0.04	17.9412	<1	60	950	0.2317
STAINLESS STEEL-310	0.25	2.0	-	24-26	19-22	-	-	-	-	-	REM.	-	-	-	0.016	0.02	-	-	0.04	12.9649	<1	60	950	0.1294
STAINLESS STEEL-309	0.20	2.0	-	22-24	12-15	-	-	-	-	-	REM.	-	-	-	0.007	0.03	-	-	0.08	14.3350	<1	60	950	0.2020

*APPROXIMATELY 100 GRAMS OF BISMUTH WAS USED IN EACH TEST

**AMOUNT UNKNOWN

COMBINATION OF POLONIUM WITH MATERIALS OF STILL CONSTRUCTION

Very little information is available on the combination of polonium with materials of still construction Investigations[23] by the Physics Section indicate that polonium forms compounds with zinc lead, platinum, nickel, silver and sodium but no compounds with gold, tantalum, iron, beryllium and aluminum were found A test[22] performed to simulate still conditions consisted of sealing one curie of polonium in a small steel container and repeatedly heating and cooling it. It was opened and heated to a high temperature to drive off the free polonium. Upon dissolving the container, 2.6 per cent of the original polonium was found. A second test consisted of condensing on and driving off polonium from a steel sample until a total of 15 curies had been so transferred Upon calorimetering the steel sample it was found to retain about one millicurie. It was concluded that retention of polonium by steel was low.

CREEP-STRENGTH AND PROTECTION AGAINST SCALING

Low-carbon steel was used as a material of construction for experimental stills until a better material could be found, although when used alone it has major disadvantages. It has low creep-strength at elevated temperatures; is subject to rapid atmospheric corrosion at elevated temperatures, and is attacked by bismuth to a certain extent. The disadvantage of low creep strength tends to limit the size of still-pots so that still wall-thickness increases rapidly for stills over about eight inches inside diameter. Atmospheric corrosion on the outside of the still has been a problem. Heavy nickel-plate if properly applied offers protection from scaling of mild steel for several hundred hours at operating temperatures. Aluminum impregnation appears to offer similar protection; however, it may create problems in heat transfer as this type of surface seems to act as a refractory material. Chromium and silicon impregnation appear to be unsatisfactory and both are difficult and expensive operations Silicon-impregnated surfaces are very brittle and are damaged by thermal shock. A protective surface which promises to overcome some of the above disadvantages is that of surfacing-by-welding Test pieces of low-carbon steel enveloped in $\frac{3}{8}$-inch of type 310 stabilized stainless steel weld-stock have stood up well to thermal shock tests. In addition 310 stainless steel has a creep strength of 2300 pounds per square inch for 1 per cent creep in 10 000 hours at 1400°F as compared to approximately 100 pounds per square inch for low-carbon steel. Both literature[24] reports and our tests on surfaced samples indicate that type 310 stainless steel is resistant to scaling at 2100°F. The surfacing-by-welding process is expensive and time-consuming for large pieces

GRAPHITE FOR STILL CONSTRUCTION

Graphite[18] is another material which has not been tried for still construction here, but which warrants consideration. The use of a non-metal would involve major revisions in still design but in view of the fact that no ideal metal has been found, it may provide the best long-range solution to this problem.

CURRENT PRACTICE

Although perhaps not an ideal system, low-carbon steel with a welded type 310-Cb stainless steel covering will be used for the pilot plant still because the low-carbon steel has stood up fairly well as the interior of experimental stills and it does not appear to absorb polonium. The welded stainless steel cover provides high-temperature strength and oxidation resistance.

STILL DESIGN AND CONSTRUCTION PROBLEMS

SEALS

Faulty vacuum-tight seals were troublesome in early still designs. Attempts to use metal seals near heated zones were generally unsuccessful. However, by allowing air-cooled or water-cooled sections to isolate the seal from a hot zone, "O" ring seals proved to be fairly reliable. Since bismuth expands upon solidification, this property has been used in the sealing of bismuth flow-lines. A line sealed in this fashion usually gives an excellent vacuum seal which can be opened readily by application of heat. "Weather-head" compression fittings have been successful for some sealing applications, but were not satisfactory for sizes larger than ½ inch. A modification of this fitting is the "Swagelok" compression fitting. This type of fitting appears to give a more positive seal at elevated temperatures and has been used with success at Brookhaven National Laboratory for vacuum-tight tubing connections.

PRODUCT CONDENSERS

Product condensation and collection is a continuing design problem. Solid bismuth is a notoriously poor conductor of heat. Also, the bismuth vapor condenses as a dendritic needle-like structure which further reduces the heat-transfer characteristics of the product mass. These conditions give rise to three types of troubles: (1), the product crumbles fairly easily if sharply jarred; (2), product build-up may be limited by its poor heat-transfer property; and (3), bridging of the product to the column side-wall must be avoided in condenser design and operation.

Current condenser design provides for a cooled cylinder suspended in the heated upper portion of the column in such a fashion that an extension of the column extends a short distance into the condenser. The expanded portion of the column into which the condenser fits and the column extension provide an annulus into which the lower portion of the condenser is suspended without making contact with the hot column side-walls as shown in Figure 5. This arrangement has permitted separation of the product from liberated or introduced gases and collection of the product within the condenser which results in material balances being well within experimental counting error. However, bismuth which drops into this annular space due to spattering or thermal short-circuiting of product is difficult to remove, and if left, causes low concentration-factor results for the products of succeeding distillation runs. Condensers of this type also introduce undesirable restrictions in the vacuum system. Consequently, a study of methods of product collection should continue to be made until these conditions are corrected.

Another condenser design which is being considered would have the vacuum drawn directly through the cooled collector past baffles. There would be less chance with such a design of bismuth or polonium accumulating in the annular space.

SPARGERS

Sparger design has proven troublesome. If incorporated into the still as a permanent non-replaceable part the sparger becomes the most vulnerable spot in the still design. If incorporated as a replaceable part, problems of gas dispersion and vacuum-tight seals arise.

A sintered disk in the bottom of a still proved unreliable due to fabrication difficulties. However, a test piece with a sintered disk made to observe gas distribution within the bismuth melt showed excellent distribution. It permitted helium to pass into the melt while at the same time acting as an effective barrier with or without gas flow to the reverse flow of the molten bismuth.

A perforated disk with perforations of 0.025-inch diameter was effective. After many runs with this type of disk most of the perforations were clogged, yet no difference was noted in distillation rates or product concentration.

WELDED JOINTS

Most still failures can be attributed to welds which for one reason or another became porous after the still was put in operation. Familiarity with good welding technique is essential for the designer as well as for the welder. Common mistakes in design include lack of provision for welding room between parts; welding of unequal masses; intricate joints which cause non-continuous welding and excessive metal stressing; and the use of welded joints where a completely machined part could be used or where parts could be joined effectively by silver solder or by mechanical seals. Common mistakes in welding include improper choice of welding rod; lack of proper equipment; shallow welds; scale and flux inclusions; thermal shock; and no provision for annealing after welding. Vacuum-tight welded joints for low-carbon steel can be obtained by: (1), using either Heliarc or Sigma welding equipment; (2), providing an inert atmosphere in the interior of cylindrical parts during welding; (3), providing for 100 per cent welds instead of shallow welds; (4), using welding rod of the same composition as the stock to be welded; and (5), making provision for a slow cooling cycle if the part is not immediately annealed after welding.

SUMMARY

Early bismuth-polonium stills indicated the possibility that distillation could be developed into a practical process for the separation of polonium from bismuth. However, the first glassware-contained experiments and the first fractionating still gave fair and excellent concentration factors, respectively, at low depletion rates. The stripping still, which was operated at a higher temperature, depleted the bismuth rapidly at the expense of product concentration.

Agitation by sparging was investigated as a means of improving still performance and appeared to produce considerable benefit. Two stills employing this principle and differing only in their material of construction were built and produced excellent results. The bismuth charge was usually depleted of over 99.5 per cent of its polonium in three hours and a product concentration 150 to 1000 times that of the original charge was obtained.

Simple distillation without fractionation was investigated. Considerable work was done on the relative volatilities and vaporization rates of polonium and bismuth from their mixtures. The results obtained with small experimental units indicated that a two-stage system of simple stills of reasonable size operating on a one-day cycle could give a concentration factor of several hundred while recovering well over 99 per cent of the polonium from irradiated bismuth.

Finding a suitable material for the construction of stills has been a major problem facing this project. Resistance to molten bismuth, no affinity for polonium, and high temperature strength are some of the necessary properties. No completely satisfactory material has been located either by this Laboratory or by other sites which have investigated this problem. At our request Battelle Memorial Institute did considerable work on this phase of the project and recommended a silicon steel as having the best resistance to bismuth of the many alloys

that they tested One of the sparging stills previously mentioned was constructed of this material but gave indication of absorbing an excessive amount of polonium on the silicon steel walls Currently stills are being constructed with a low-carbon steel body with an outer layer of stainless steel applied by welding to give strength and resistance to high temperature scaling

In the process of constructing and operating experimental stills considerable information and experience has been gained on the various phases of still design. High temperature seals product condensers sparging inlets and welded joints have all presented special problems which have been solved to a reasonable degree

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