

**Bureau of Mines
Report of Investigations 5243**



**SELECTIVE EXTRACTION OF MERCURY
AND ANTIMONY FROM CINNABAR-STIBNITE ORE**

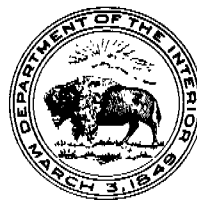
BY E. G. ERSPAMER AND R. R. WELLS

United States Department of the Interior — September 1956

**SELECTIVE EXTRACTION OF MERCURY
AND ANTIMONY FROM CINNABAR-STIBNITE ORE**

BY E. G. ERSPAMER AND R. R. WELLS

* * * * * **Report of Investigations 5243**



**UNITED STATES DEPARTMENT OF THE INTERIOR
Fred A. Seaton, Secretary
BUREAU OF MINES
Marling J. Ankeny, Director**

Work on manuscript completed November 1955. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Report of Investigations 5243."

September 1956

SELECTIVE EXTRACTION OF MERCURY AND ANTIMONY
FROM CINNABAR-STIBNITE ORE

by

E. G. Erspamer^{1/} and R. R. Wells^{2,3/}

CONTENTS

	<u>Page</u>
Summary	1
Introduction	1
Concentration of mercury ores	2
Previous laboratory studies of Red Devil ore	4
Current investigations	5
Scope	5
Mineral-dressing studies	5
Character of the ore	5
Physical	5
Chemical	5
Preliminary tests	6
Screen analysis	6
Heavy-liquid test	6
Methods of concentration	6
Gravity concentration	6
Bulk flotation	7
Selective flotation	8
Discussion	9

^{1/} Formerly metallurgist, Bureau of Mines, Region I, Juneau, Alaska.

^{2/} Supervising metallurgist, Bureau of Mines, Region I, Juneau, Alaska.

^{3/} In preparing this report, the authors were assisted by J. V. Batty and G. M. Potter, metallurgists, Intermountain Experiment Laboratory, Salt Lake City, Utah, and C. T. Baroch, metallurgist, Boulder City, Nev.

CONTENTS (Con.)

	<u>Page</u>
Current investigations (Con.)	
Furnace-reduction studies	9
Experimental procedure	9
Results	9
Excess air	9
Limited air	9
Discussion	10
Hydrometallurgical studies	10
Library research	10
Leaching	11
Results	11
Precipitation	13
Discussion	13
Bibliography	13

TABLES

1. Chemical analysis of Red Devil ore	5
2. Spectrographic analysis	5
3. Screen analysis	6
4. Jig and table test	7
5. Locked flotation test	7
6. Selective flotation, Red Devil ore	8
7. Leaching tests on 1:1 cinnabar-stibnite mixtures	11
8. Leach tests on bulk flotation concentrate	12

ILLUSTRATION

Fig.

1. Location map, Kuskokwim mercury area	3
---	---

SUMMARY

Laboratory investigations were made by the Bureau of Mines on ore containing the sulfides of both mercury and antimony to develop a method or methods for the economic recovery of mercury metal and the concurrent recovery of antimony as metal or salts. If standard mercury-recovery techniques are applied to such ores, the antimony content interferes with the effective production of mercury metal; furthermore, the antimony is lost.

This report presents the results of tests on a sample of cinnabar-stibnite ore from the Red Devil mine near Sleitmute, Alaska. Red Devil ore was chosen for the investigation because it is purported to be typical of ores of the Kuskokwim River area, which, in their aggregate, constitute large potential reserves of mercury and antimony. Studies included petrographic, spectrographic, and chemical analyses, gravity-separation tests, bulk flotation of mercury and antimony sulfides, differential flotation, leaching, and furnacing of crude ore and of flotation concentrate.

Results of this investigation indicate that bulk flotation of sulfides, followed by furnacing of the flotation concentrate with a carefully regulated admission of air, would yield an overall recovery of more than 95 percent of the mercury in the ore and would permit possible recovery of antimony from the furnace calcine. Similar treatment is reported to have been employed successfully on livingstonite ore from Guerrero, Mexico (15).^{4/}

Results of preliminary hydrometallurgical tests indicated that leaching of cinnabar-stibnite ores or concentrates with sodium sulfide solution is a potential means of obtaining separate mercury and antimony products.

INTRODUCTION

Quicksilver has long been noted as a metal with tremendous and sudden price fluctuations. Recent fluctuations in price have included an increase from \$75 per 76-pound flask shortly before World War II to \$196 per flask during that war, a sharp drop to \$70 per flask in June 1950, and an equally sharp rise to \$233 per flask by January 1951. Since 1951 the price has maintained a high level; it has not dropped below \$180 per flask and climbed as high as \$325 per flask in October 1954.

The rate of increase in consumption of quicksilver is well illustrated by the following quotation from C. N. Schuette (25, p. 326).

^{4/} Underlined numbers in parentheses refer to citations in the bibliography at the end of this report. Page references refer to pages in the citation and not in this report.

In the five pre-World War II years of 1936 through 1940, the average annual consumption was 27,340 flasks, the peak being 35,000 flasks in 1937. In the five World War II years of 1941 through 1945, the average annual consumption was 50,866 flasks, the peak year being 1945 with a consumption of 62,429 flasks. In the five post-World War II years of 1946 through 1950, the average annual consumption was 40,491 flasks, 1950 consumption reaching a 49,215-flask peak.

The two factors - increased consumption and increased average price - have stimulated domestic quicksilver production and have renewed interest in the mercury deposits of southwestern Alaska, especially those of the Kuskokwim Basin. (See fig. 1.) Field examinations, coupled with significant ore discoveries made as a result of an exploration program at the Red Devil mine during the summer of 1955, indicate that the Kuskokwim area has large potential reserves of mercury ore.

In some Kuskokwim deposits cinnabar is associated intimately with significant quantities of stibnite. Arsenic minerals are present in smaller amounts. The presence of these volatile impurities is detrimental to economic recovery of quicksilver by standard mercury-recovery techniques. At the Red Devil plant it was determined that nearly complete oxidation of the antimony and arsenic was required to effect good recovery of quicksilver. A large amount of the oxides of these impurities therefore was collected in the condensing system. As a result of the presence of the bulky oxide precipitate, treatment of the soot for recovery of mercury was difficult and costly.

No records of mercury losses at the Red Devil recovery plant were maintained. It is generally estimated, however, that recovery has averaged less than 70 percent and has been especially poor on ores of high antimony content.

The laboratory study was conducted with a twofold purpose. First, it was desired to devise a method that would effect more complete and more economic extraction of mercury from the ore. Second, it was deemed desirable to determine the feasibility of making an antimony byproduct and thus to utilize a commodity that is wasted by the standard furnacing methods now used.

CONCENTRATION OF MERCURY ORES

Most mercury ores are roasted directly or are retorted for recovery of the metal without prior concentration. Recoveries are high; costs usually are nominal. Schuette (25, p. 325) reports that the New Almaden mine in California operated at a profit during World War II on ore averaging only 3 pounds of mercury per ton.

Walter W. Bradley (1) conducted a large number of laboratory concentration tests in 1919; he concluded that the ultimate decision between straight furnace reduction and combined concentration and reduction treatment was a matter of comparative costs and comparative extractions and that usually the combined treatment had doubtful economic value. Under most conditions, it is probable that the cost of the added grinding and concentrating operations is greater than the saving inherent in roasting only a portion of the ore. For this reason, aside from a few small operations, concentration of mercury ores never has been accepted for plant practice.

When unusual conditions exist, however, a combined treatment process deserves consideration. In the Kuskokwim area the cost of erecting and equipping a large plant and the cost of fuel for roasting are major items. The possibility exists, therefore, of saving enough to offset the cost of concentration, provided the concentration is efficient both in recovery and in ratio of concentration.

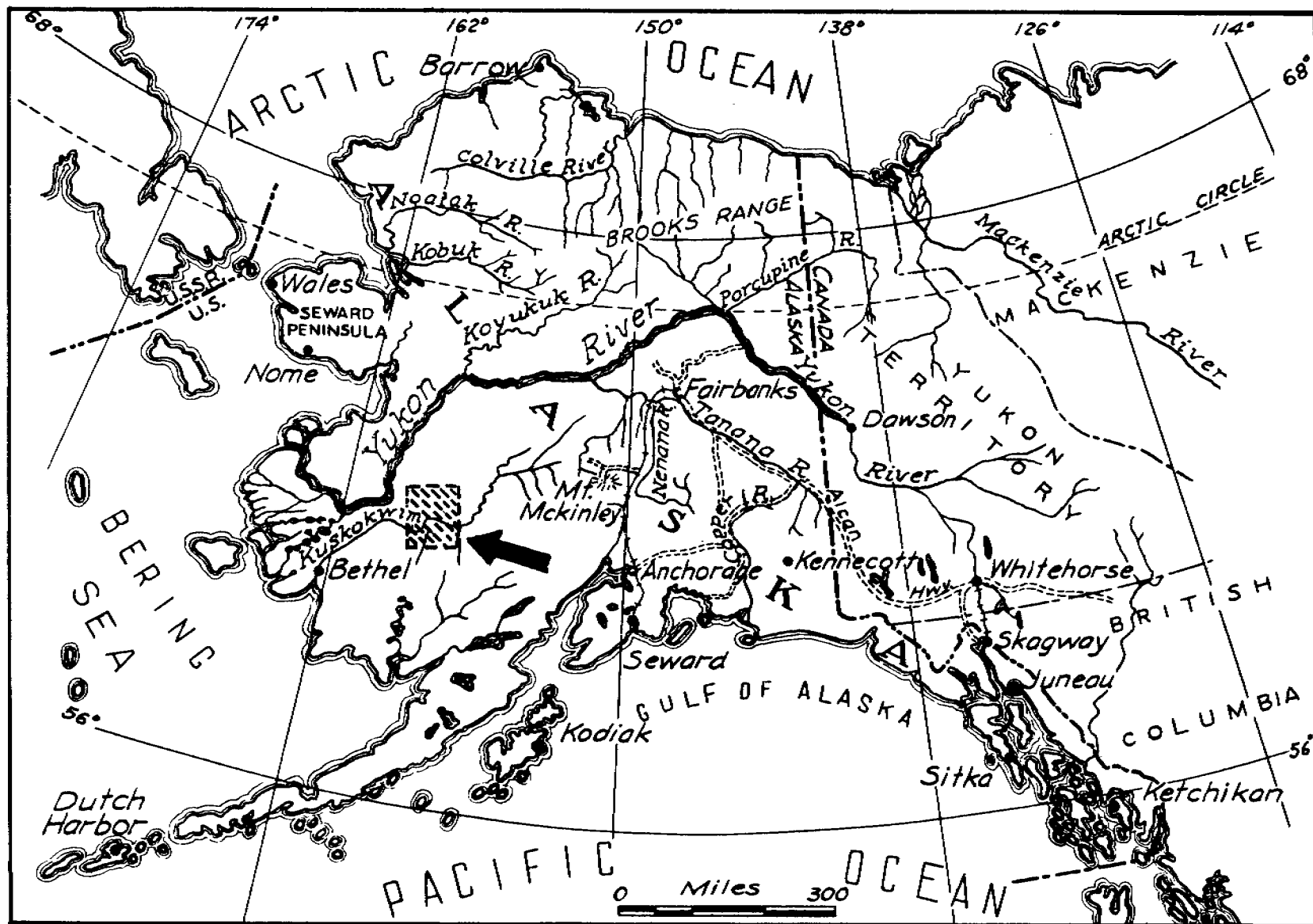


Figure 1. - Location map, Kuskokwim mercury area 

In spite of the high specific gravity of cinnabar, gravity methods rarely are applicable for concentrating mercury ores. Cinnabar slimes readily; thus, considerable loss is involved if the slimes are discarded. Addition of slimes to the gravity concentrate results in a low-grade product containing large amounts of fine gangue; such products are difficult to filter and dry and, in addition, usually present difficulties in subsequent reduction treatment.

Laboratory work by Shaffer, Newton, and Fahrenwald (27), Rey and Brevers (23), Wells (41), and others indicates that cinnabar is readily amenable to flotation. Tailings containing 0.2 to 1.0 pound of Hg per ton are not uncommon. High-grade concentrates, amenable to reduction by retorting or roasting, usually are obtained.

PREVIOUS LABORATORY STUDIES OF RED DEVIL ORE

Early in 1947 a sample of cinnabar-stibnite ore from the Red Devil mine was submitted to the Salt Lake City laboratories to determine a practical method of separating the two minerals into a furnaceable mercury concentrate and a marketable antimony concentrate. Unfortunately, the sample, taken from a high-grade ore lens, was not representative of run-of-mine ore. Nevertheless, a large number of tests were made which resulted in the development of bulk and selective flotation techniques that served as a basis for the current investigation.

The sample tested at Salt Lake City assayed 9.43 percent Hg and 16.6 percent Sb. Cinnabar and stibnite occurred in a gangue consisting chiefly of quartz and kaolin, with a small amount of dolomite. The gangue rock was silicified and impregnated with fine needles of pyrite. Grinding to minus-100-mesh liberated the cinnabar and most of the stibnite.

Gravity methods of concentration yielded only partial separation of cinnabar and stibnite.

A sample of the ore was ground to approximately 65-mesh with sodium cyanide to depress pyrite; a cinnabar-stibnite bulk concentrate was floated with a higher xanthate collector. Lead acetate was used as an activator, and an alcohol frother was employed. The rougher concentrate was cleaned once using small additional amounts of collector and activator. The cleaned bulk concentrate contained about one-third of the weight of the original ore, 97.8 percent of the total mercury, and 94.7 percent of the total antimony; it assayed 27.1 percent Hg and 47.4 percent Sb.

A selective flotation process for making separate cinnabar and stibnite products was developed after considerable investigation. A dichromate salt and a promoter (Minerex No. 194) were added to the grinding circuit. Stibnite remained depressed, but the cinnabar was floated readily. Sulfuric acid and lead acetate were added to reactivate the stibnite, and an antimony product was floated using a higher xanthate and an alcohol frother. Each concentrate was cleaned once. Applying this method to ore ground to approximately 80-mesh, 96.0 percent of the mercury in the ore was recovered in a cinnabar concentrate that assayed 80.3 percent Hg and 1.3 percent Sb. The antimony product contained 80.7 percent of the antimony; it assayed 0.82 percent Hg and 62.3 percent Sb. The mercury product contained 11.6 percent of the original weight; the antimony concentrate contained 20.8 percent of the original weight.

CURRENT INVESTIGATION

Scope

This investigation was directed toward a general survey of possible methods of selective recovery of mercury and antimony rather than toward detailed study of any one method. To this end, preliminary studies were made of mineral dressing, furnace reduction, and hydrometallurgical treatments. The presentation of data and the discussion of results from each type of treatment are reported separately.

Mineral-Dressing Studies

Character of the Ore

The ore for this investigation was selected carefully to obtain a sample as nearly as possible representative of the known ore body, both as to mineralogical and chemical content.

The material as received at the laboratory was crushed and sampled to obtain representative fractions for petrographic, spectrographic, and chemical analyses.

Physical

The sample contains essentially quartz and sericite, with some altered feldspar, carbonaceous matter, and stibnite and less cinnabar and limonite. Small amounts of chlorite, realgar, calcite, and kaolinite are present, as well as very small amounts of gypsum, amphibole, stibiconite, and pyrite.

Cinnabar and stibnite are associated closely with the realgar and with each other. Some of the cinnabar occurs as inclusions in stibnite, and some of the stibnite is included in cinnabar. The stibnite and cinnabar are essentially freed from gangue minerals in the plus-100-mesh fraction; some of the stibnite, however, is so fine grained that it remains locked, even in the minus-200-mesh fraction.

Chemical

The chemical analysis is given in table 1.

TABLE 1. - Chemical analysis of Red Devil ore

Assay, percent				
Hg	Sb	As	Fe	SiO ₂
1.6	2.7	0.73	3.5	45.6

A semiquantitative spectrographic analysis showed the presence and approximate amounts of the metals listed in table 2. Any other elements, if present, are in quantities less than the minimum detectable by the routine method employed.

TABLE 2. - Spectrographic analysis

Ba	Al	Sb	As	Be	Ca	Cu	Mg	Cr	Fe	Mn	Ni	Si	Ti	V	B
F	C/	C	C-	F	E	E	D	F	C/	D	E	A	E	E	E

Legend: A - over 10 percent E - 0.01 to 0.1 percent
 B - 5 to 10 percent F - 0.001 to 0.01 percent
 C - 1 to 5 percent G - less than 0.001 percent
 D - 0.1 to 1 percent

Preliminary Tests

Screen Analysis

A representative portion of the ore was roll-crushed to minus-10-mesh and subjected to wet-screen analysis to determine the distribution of the mineral values in relation to particle size using standard Tyler sieves. Results of the screen analysis are shown in table 3.

TABLE 3. - Screen analysis

Product	Weight-percent	Assay, percent		Distribution, percent	
		Hg	Sb	Hg	Sb
Plus-20-mesh	25.82	1.52	2.42	22.7	24.2
20/35	19.34	1.80	2.60	20.1	20.0
35/48	7.32	1.98	2.79	8.4	7.9
48/65	6.89	1.96	2.99	7.8	8.0
65/100	5.46	1.90	2.74	6.0	5.8
100/200	8.09	2.20	2.94	10.3	9.2
Minus-200-mesh sand	10.21	3.40	2.98	20.0	11.8
Slime	16.87	.48	2.01	4.7	13.1
Calculated head	100.00	1.7	2.6	100.0	100.0

The data in table 4 show that mineral liberation is incomplete in the particle sizes for which gravity processes are applicable. The distribution of antimony in each size fraction parallels closely the weight of the fraction; this demonstrates intimate association of stibnite with other minerals throughout the entire size range. A similar relationship exists between fraction weight and mercury content in the material coarser than 100-mesh; this indicates that cinnabar is liberated only in the finer sizes. The difference in liberation of cinnabar and stibnite is further shown by the fact that the minus-200-mesh slime contained 13.1 percent of the total antimony but only 4.7 percent of the total mercury.

Heavy-Liquid Test

To explore further the amenability of the ore to specific-gravity separation processes, a heavy-liquid test was made. A representative portion of the ore was roll-crushed to 10-mesh and screened at 35-mesh. The minus-10-, plus-35-mesh material was separated successively at specific gravities of 2.67 and 2.54 in tetrabromoethane. The minus-35-mesh portion was not treated.

The results of this test corroborated the findings of the petrographic examination and the screen analysis of the ore.

Methods of Concentration

Gravity Concentration

The possibility remained that gravity separation could be employed as a preliminary concentration step to remove a coarse concentrate. The gravity tailings would represent a reduced tonnage for fine grinding and subsequent beneficiation processes.

A representative portion of the ore was roll-crushed to minus-1/4-inch and screened at 10-, 20-, 48-, 100-, and 200-mesh. The 1/4-inch to 10-mesh portion was jigged in a laboratory Harz-type jig. The remaining size fractions were tabled

successively on a laboratory Wilfley table. Results of the combined jig-table tests are shown in table 4. The composite concentrate contained 16.3 percent Hg and 18.0 percent Sb, with a recovery of 70.1 percent of the total mercury and 53.0 percent of the total antimony. This product represented only 7.5 percent of the original sample weight; no tailing product obtained was low enough in mercury and antimony content to reject without further treatment. Therefore, a negligible weight rejection was achieved by gravity concentration.

TABLE 4. - Jig and table test

Product	Weight-percent	Assay, percent		Distribution, percent	
		Hg	Sb	Hg	Sb
Jig concentrate	5.06	9.68	15.6	28.2	31.1
Table concentrate	2.41	30.2	23.0	41.9	21.9
Jig middling	12.61	.89	1.54	6.4	7.7
Table middling	3.30	1.15	4.45	2.2	5.8
Jig tailing	38.46	.43	.61	9.5	9.3
Table tailing	29.40	.45	1.12	7.6	13.0
Slime	8.76	.84	3.25	4.2	11.2
Calculated head	100.00	1.74	2.53	100.0	100.0
Composite concentrate	7.47	16.3	18.0	70.1	53.0
Composite middling	15.91	.94	2.14	8.6	13.5
Composite tailing	67.86	.44	.83	17.1	22.3

Bulk Flotation

The necessity for finer grinding to unlock cinnabar and stibnite from gangue minerals dictated the use of flotation techniques on Red Devil ore. Batch tests were made on samples ground to minus-65- and minus-100-mesh, using various reagent combinations to float a bulk sulfide concentrate. The best procedure was determined to be grinding with sodium cyanide to essentially minus-65-mesh, conditioning with lead acetate, and rougher floating with American Cyanamid Reagent 301 and Frother 63. The rougher concentrate was cleaned once. Employing this procedure, a locked test was made on 15 one-kilogram samples; cleaner tailings were added to the next successive rougher pulp. Results are shown in table 5. The bulk cinnabar-stibnite concentrate contained 23.4 percent Hg and 30.7 percent Sb, with a recovery of 96.9 percent of the total mercury and 76.1 percent of the total antimony in the ore. Even with a 65-mesh grind, approximately 20 percent of the antimony remains locked with gangue minerals.

More than 93 percent of the total weight of the ore was rejected as tailing; only 6.32 percent would require furnacing or retorting for the production of mercury metal.

TABLE 5. - Locked flotation test

Product	Weight-percent	Metallurgical data		Distribution, percent	
		Assay, percent		Hg	Sb
		Hg	Sb		
Cleaner concentrate	6.32	23.4	30.7	96.9	76.1
Rougher tailing	93.68	0.05	0.65	3.1	23.9
Calculated head	100.00	1.53	2.55	100.0	100.0

TABLE 5. - Locked flotation test (Con.)

Operating data						
Circuit	Time, min.	pH	NaCN	Pb acetate	Reagent 301	Frother 63
Grind			1.0	-	-	-
Conditioner	5	6.0	-	1.5	0.2	0.08
Rougher	7		-	-	.2	-
Cleaner	3		-	-	-	-
Total			1.0	1.5	.4	.08

Selective Flotation

A long series of tests was run in the attempt to produce separate mercury and antimony flotation concentrates. No results approached those obtained by the Salt Lake laboratory from the high-grade sample tested there. The dichromate depressant technique developed by the Salt Lake staff, however, appeared to be superior to any other method investigated, although the required consumption of sodium dichromate was excessively high for treatment of the lower grade material.

The best selective flotation results were obtained by grinding minus-10-mesh ore with sodium dichromate and promoter; a rougher mercury concentrate was floated and was cleaned twice. The mercury rougher tailing was reground, and an antimony concentrate was floated in an acid circuit. The antimony product was cleaned twice. Like cleaner tailings were combined for assay. Results are summarized in table 6.

TABLE 6. - Selective flotation, Red Devil ore

Metallurgical data					
Product	Weight-percent	Assay, percent		Distribution, percent	
		Hg	Sb	Hg	Sb
Hg cleaner conc.	1.10	78.72	2.3	62.2	1.0
Hg cleaner tailings	5.72	6.09	13.4	25.0	30.0
Sb cleaner conc.	1.72	5.54	49.4	6.8	33.3
Sb cleaner tailings	5.02	1.24	4.5	4.4	8.9
Rougher tailings	86.44	1/0.05	0.79	1.6	26.8
Calculated heads	100.00	1.4	2.6	100.0	100.0
Calculated Hg rougher conc.	6.82	17.8	11.6	87.2	31.0

Operating data								
Circuit	Time, min.	pH	Na ₂ Cr ₂ O ₇	H ₂ SO ₄	Pb acetate	Collector 1 ^{2/}	Collector 2 ^{3/}	Frother ^{4/}
Grind	10		6.0			0.12		
Hg rougher ..	4	8.5	6.0					0.08
Hg cleaner 1.	4		3.0					
Hg cleaner 2.	3		6.0					.04
Regrind	5							
Sb rougher ..	5	4.9		2.0	0.3		0.15	.04
Sb cleaner 1.	3							.04
Sb cleaner 2.	3							.04
Total			21.0	2.0	0.3	0.12	0.15	0.24

1/ Less than.

2/ Collector 1 - Minerec 27.

3/ Collector 2 - American Cyanamid reagent 301.

4/ Frother - Dowfroth 250.

Discussion

By selective flotation, 87.2 percent of the total mercury was recovered in a rougher concentrate that assayed 17.8 percent Hg and 11.6 percent Sb. Cleaning improved the grade to 78.72 percent Hg and 2.3 percent Sb, but with a sharp decrease in mercury recovery; only 62.2 percent of the total mercury was recovered in the cleaner concentrate. A recovery of 33.3 percent of the total antimony was made with a grade of 49.4 percent Sb and 5.54 percent Hg.

In no test was selectivity sharp enough to allow production of an antimony concentrate low in mercury content; 10 to 20 percent of the mercury reported in the antimony products. Thus, as both the mercury and antimony fractions would require further treatment to yield end products, it was concluded that application of selective flotation to Red Devil ore is not promising.

Furnace-Reduction Studies

Experimental Procedure

Experiments were made on crude ore and on bulk flotation concentrate to volatilize the cinnabar and to retain the stibnite in the furnace calcine. A laboratory horizontal-tube furnace was employed for this work. Charges were heated without rabbling in 10-gram alundum boats. Air was regulated by applying suction to one end of the furnace tube. Extraction calculations were based solely on weight and analysis of the residue after calcining; no attempt was made to collect the furnace fume. The limitation of charge size coupled with accuracy limitation of analyses, yielded erratic results. The trend of recoveries, however, was indicative enough to make general conclusions.

Results

Excess Air

For the purpose of studying the results that would be obtained by standard mercury-recovery methods, a series of tests was run with a plentiful supply of air to oxidize the cinnabar and to remove the mercury as volatilized metal. Results on both crude ore and concentrate indicated mercury extractions of 98 to nearly 100 percent, but the results also demonstrated that this method of roasting converted 25 to 50 percent of the antimony to antimony oxide. These laboratory results agreed with the results obtained at the Red Devil plant, where considerable trouble was experienced with large amounts of antimony oxides entering the condensing system with the volatilized mercury.

Limited Air

A series of tests was run to determine the effect of limited air admission to the furnace. It was found that oxidation of antimony could be minimized by regulating the air supply. The bulk of the mercury was removed as volatilized cinnabar, which would require treatment in an oxidizing atmosphere to yield mercury metal.

Results of numerous tests, conducted on bulk concentrate between 450° and 650° C., showed consistent mercury extractions of 99.9 percent, with a retention of 83 to 93 percent of the antimony in the calcine. A similar series of tests on minus-10-mesh crude ore showed extractions of more than 98.5 percent of the mercury and a retention of 80 to 90 percent of the antimony. Within the 450° to 650° C. range the temperature of reduction did not appear to be a significant factor.

The results of the furnacing tests indicate that, with more precise control of air supply than was possible with the equipment used, a nearly complete separation of mercury and antimony can be made.

Discussion

The results of the laboratory-scale furnacing tests on bulk flotation concentrate suggest the possibility of applying a recovery method described by H. B. Menardi (15). Menardi's small plant at El Segundo, Calif., was used to produce separate mercury and antimony products from livingstonite ($\text{HgS} \cdot 2\text{Sb}_2\text{S}_3$) flotation concentrates from the Huitzuco deposit, Guerrero, Mexico (26). The concentrate was heated in a concurrently fired rotary kiln with careful regulation of air to produce volatilized cinnabar and to prevent excessive oxidation of stibnite. The volatilized cinnabar was oxidized in a combustion chamber to produce mercury vapor, which was condensed to obtain metallic mercury. The stibnite-rich calcine was smelted and refined to produce antimony metal. Roasting of cinnabar ores in concurrently fired furnaces has been investigated further and has been employed successfully on a large scale by the Bradley Mining Co. at its Reed and Sulfur Bank properties (11).

Assuming that controlled air-furnace treatment would give selective extractions equal to those indicated by the laboratory tests and assuming that plant flotation would yield recoveries equivalent to laboratory flotation tests, an overall recovery of 97 percent of the mercury and 68 percent of the antimony could be expected from combined flotation-furnacing treatment of Red Devil ore.

Further investigation and detailed study, preferably on a small, continuous scale, would be required, however, to prove the practicability and economic feasibility of applying Menardi's process, or modification thereof, to Red Devil concentrate.

Hydrometallurgical Studies

Library Research

A survey of the literature revealed no mention of previous application of the hydrometallurgical methods to ores containing both mercury and antimony. Leaching methods have been employed, however, on ores of each metal.

In one instance, mercury was recovered from amalgamation tailings by leaching in a solution of sodium sulfide and sodium hydroxide. This process was described by Thornhill (34). Experimental work using the process on mercury ores was done by Bradley (1). Concerning antimony, Van Arsdale (36, p. 29) states that:

Stibnite is soluble in alkali sulfides or hydroxides, and a pure antimony sulfide can be recovered from the resulting solutions by precipitation with carbon dioxide or sulfur dioxide. The method has yet to be tested on a plant scale.

Mercuric sulfide is reported to be insoluble in caustic soda and potash solutions but readily soluble in sodium or potassium sulfide to form a complex thio-compound that is completely hydrolyzed into mercuric sulfide by dilution with water (35, p. 119).

Leaching

For this investigation the initial laboratory leaching tests were made on synthetic 1-to-1 mixtures of pure cinnabar and stibnite. A bulk flotation concentrate that contained 23.4 percent Hg and 30.7 percent Sb was used for a subsequent series of tests. Lixiviants were sodium sulfide and sodium hydroxide, used separately and in mixtures of both; one cursory test was performed in which concentrated hydrochloric acid was the lixiviant.

Ten-gram samples were leached at atmospheric pressure with various concentrations of leaching agent. Other variables were temperature of the pulp, weight ratio of lixiviant to charge, and duration of leach. The pulps were agitated continuously during the leaching cycles by an electric stirrer. After digestion the slurries were filtered on a suction filter. The residues were washed and dried; residues and filtrates were submitted for chemical analysis. All leaching tests were single-stage.

Results

Data obtained from leaching tests on cinnabar-stibnite mixtures are shown in table 7.

TABLE 7. - Leaching tests on 1:1 cinnabar-stibnite mixtures

Time, min.	Lixiviant	Strength, percent	Quantity, ml.	Temp., °C.	Extraction, percent of total	
					Hg	Sb
10	NaOH	5	600	20	1.8	91.7
10	Na ₂ S·5H ₂ O	3	400	20	1.0	97.3
10	(Na ₂ S·5H ₂ O NaOH	(2 1	400	20	1.0	97.1
10	NaOH	3	400	20	1.0	86.5
10	(Na ₂ S·5H ₂ O NaOH	(1 2	400	20	1.0	96.7
15	NaOH	5	600	20	1.8	88.4
20	NaOH	5	600	20	1.8	89.6
10	NaOH	10	600	20	15.2	75.9
15	NaOH	10	600	20	7.8	86.1
20	NaOH	10	600	20	11.7	94.6
15	Na ₂ S·5H ₂ O	5	600	20	4.5	97.4
20	Na ₂ S·5H ₂ O	5	600	20	5.3	93.5
10	Na ₂ S·5H ₂ O	10	600	20	99.9	87.3
20	Na ₂ S·5H ₂ O	10	600	20	99.9	86.8
35	Na ₂ S·5H ₂ O	10	600	20	99.6	89.7
180	HCl	Concentrated	600	20	1.0	99.4

Sodium hydroxide and sodium sulfide, in concentrations of 5 percent or less, both dissolve antimony selectively from mixtures of pure cinnabar and stibnite; sodium sulfide was slightly more effective than sodium hydroxide. At 3-percent concentrations mixed sodium sulfide-sodium hydroxide leach solutions gave results similar to those obtained with sodium sulfide alone under similar conditions. Ten-percent solutions of sodium hydroxide dissolved 7 to 15 percent of the mercury; similar concentration of sodium sulfide effected nearly complete solution of the mercury.

One cursory test was made in which a mixture of the pure sulfides was leached in concentrated hydrochloric acid. The concentrated acid dissolved approximately 99 percent of the total antimony and only 1 percent of the total mercury. This method was not pursued further because concentrated hydrochloric acid would be difficult to handle in a leaching plant. Continued improvements in corrosion-resistant equipment, however, might make this of more than academic interest in the future.

The facts that elevated temperatures were not required for dissolution of the stibnite and that only weak solutions and a relatively short contact time were necessary indicated that the process warranted further study. Therefore tests were initiated on the bulk flotation concentrate. Table 8 shows the results obtained.

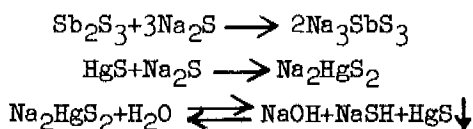
TABLE 8. - Leach tests on bulk flotation concentrate

Time, min.	Lixiviant	Strength, percent	Quantity, ml.	Temp., °C.	Extraction, percent of total	
					Hg	Sb
5	Na ₂ S·5H ₂ O	3	400	20	5.8	48.1
10	Na ₂ S·5H ₂ O	3	400	20	3.9	59.4
15	Na ₂ S·5H ₂ O	3	400	20	7.2	56.5
60	Na ₂ S·5H ₂ O	3	400	20	4.2	81.0
5	Na ₂ S·5H ₂ O	5	400	20	4.1	63.6
10	Na ₂ S·5H ₂ O	5	400	20	6.4	81.5
15	Na ₂ S·5H ₂ O	5	400	20	6.2	77.1
60	Na ₂ S·5H ₂ O	5	400	20	5.9	94.3
5	Na ₂ S·5H ₂ O	5	400	60	7.1	86.9
10	Na ₂ S·5H ₂ O	5	400	60	5.9	87.8
15	Na ₂ S·5H ₂ O	5	400	60	9.8	83.1
60	Na ₂ S·5H ₂ O	5	400	60	12.3	95.5
5	Na ₂ S·5H ₂ O	10	400	20	16.8	92.7
10	Na ₂ S·5H ₂ O	10	400	20	16.2	90.9
15	Na ₂ S·5H ₂ O	10	400	20	18.0	81.9
60	Na ₂ S·5H ₂ O	10	400	20	30.5	95.9
165	NaOH	6	200	20	38.6	49.9
165	NaOH	8	200	20	36.9	61.0
165	NaOH	10	200	20	58.2	80.7
360	NaOH	4	100	20	.4	31.3
1,140	NaOH	4	200	20	35.5	30.9
165	NaOH	6	200	70	27.7	40.5
165	NaOH	10	200	70	45.7	73.9
165	NaOH	6	200	80	59.0	60.1
15	NaOH	4	200	99	8.3	93.4
15	NaOH	6	200	99	13.5	96.3
15	NaOH	8	200	99	28.1	96.9
15	NaOH	10	200	99	36.7	95.1

Table 8 shows that greater difficulty was experienced with both sodium sulfide and sodium hydroxide in obtaining selective extractions of the stibnite from the bulk flotation concentrate than from synthetic mixtures. Sodium sulfide was definitely superior to sodium hydroxide as a differential leaching agent for the flotation concentrate. With a 60-minute contact time in a 5-percent sodium sulfide solution at room temperature, approximately 6 percent of the total mercury and 94 percent of the total antimony were dissolved. The most effective leaching conditions, using sodium hydroxide, were a 15-minute contact time in a 4-percent solution at the boiling point. Under these conditions approximately 8 percent of the total mercury and 93 percent of the total antimony were dissolved.

Precipitation

The following chemical reactions are believed to be involved in leaching cinnabar and stibnite with sodium sulfide:



In a dilute solution of sodium sulfide both the cinnabar and stibnite are dissolved to form soluble thio-compounds; the mercury thio-compound, however, is hydrolyzed immediately to a mercuric sulfide precipitate. The mercury sulfide is removed by filtration; the antimony-pregnant solution reportedly can be treated with carbon dioxide or sulfur dioxide to recover a purified antimony sulfide (35). Zinc, lead, tin, and other metals are reported to precipitate metallic antimony from solutions of antimony compounds (35). This presents an alternate method of recovery if metallic antimony, rather than the sulfide, should be an economically preferable commodity.

Discussion

This investigation has shown on a laboratory scale that leaching of cinnabar-stibnite ores with sodium sulfide is a potential means of producing separate mercury and antimony concentrates.

The limited scope of this investigation did not permit study of the precipitation of antimony from the leach solutions, although several possibilities have been suggested. No attempt was made to investigate regeneration of the lixiviant, although regeneration would be desirable economically. The pregnant leaching solutions contain sodium hydrosulfide and sodium hydroxide in addition to the antimony thio-compound. It appears within the realm of possibility that sodium sulfide for recycling in the process could be obtained from the hydrosulfide and hydroxide. Further work would be necessary to test the validity of these assumptions.

BIBLIOGRAPHY

1. BRADLEY, W. W. Quicksilver Resources of California. California State Mining Bureau Bull. 78, 1918, 389 pp.
2. BRADLEY, WORTH. Method and Cost of Recovering Quicksilver From Low-Grade Ore at the Reduction Plant of the Sulfur Bank Syndicate, Clearlake, Calif. Bureau of Mines Inf. Circ. 6429, 1931, 17 pp.
3. BRAY, J. L. Nonferrous Production Metallurgy. John Wiley & Sons, Inc., 1947, pp. 376-386.
4. CADY, W. M., WALLACE, R. E., HOARE, J. M. and WEBBER, E. J. The Central Kuskokwin Region, Alaska. Geol. Survey Prof. Paper 268, 1955, 132 pp.
5. DENVER EQUIPMENT CO. Compañía Mercurio en Sain Alto and Beneficiadora de Mercurio. S A. Bull. M4-B24, July 1942.
6. DUSCHAK, L. H., and ACHUETTE, C. N. Fume and Other Losses in Condensing Quicksilver From Furnace Gases. Bureau of Mines Tech. Paper 96, 1918, 29 pp.

7. DUSCHAK, L. H. The Metallurgy of Quicksilver. Bureau of Mines Bull. 222, 1925, 173 pp.
8. _____. Improvements in the Metallurgy of Quicksilver. AIME Tech. Pub. 264, 1940, 37 pp.
9. FROLLI, A. W. Mining and Reduction Methods and Costs at the Oceanic Quicksilver Mine, Cambria, San Luis Obispo County, Calif. Bureau of Mines Inf. Circ. 6950, 1937, 13 pp.
10. GAUDIN, A. M. Flotation. McGraw-Hill Book Co., Inc., 1932, pp. 338-342.
11. HALL, R. G., and BRADLEY, W. Concurrent Firing at Sulfur Bank and Reed Quicksilver Plants. AIME Tech. Pub. 1889, Metals Technol., December 1945, 11 pp.
12. HAYWARD, C. R. An Outline of Metallurgical Practice. D. Van Nostrand Co., 3d ed., 1952, pp. 333-349.
13. KNAPP, L. E. Report of the Governor of Alaska for the Fiscal Year 1881-1882, p. 31.
14. LIDDELL, D. M. Handbook of Nonferrous Metallurgy. McGraw-Hill Book Co., Inc., 1945, pp. 125-138, 473-516.
15. MENARDI, H. B. Reduction of Livingstonite Concentrate. AIME Tech. Pub. 1042, Metals Technol., February 1939, 8 pp.
16. MERTIE J. B., Jr. Mineral Deposits of the Ruby-Kuskokwim Region, Alaska. Geol. Survey Bull. 864-C, 1936, pp. 115-245.
17. MERTIE, J. B., Jr., and HARRINGTON, G. L. The Ruby-Kuskokwim Region, Alaska. Geol. Survey Bull. 754, 1924, 129 pp.
18. MOOREHEAD, W. R. Methods and Costs of Mining Quicksilver Ore at the New Idria Mine, San Benito County, Calif. Bureau of Mines Inf. Circ. 6462, 1931, 14 pp.
19. PETROF, IVAN. Report on Population, Industry and Resources of Alaska, 1884, 189 pp.
20. RANDALL, M., and HUMPHREY, H. B. New Process for Controlling Mercury Vapor. Bureau of Mines Inf. Circ. 7206, 1942, 10 pp.
21. RUTLEDGE, F. A. Investigation of the Rainy Creek Mercury Prospect, Bethel District, Kuskokwim Region, Southwestern Alaska. Bureau of Mines Rept. of Investigations 4361, 1948, 7 pp.
22. _____. Investigation of Mercury Deposits, Cinnabar Creek Area, Georgetown and Akiak Districts, Kuskokwim Region, Southwestern Alaska. Bureau of Mines Rept. of Investigations 4719, 1950, 9 pp.
23. REY, M. and BREVERS, H. Differential Flotation of an Arsenical Quicksilver Ore. AIME Tech. Pub. 1264, Min. Technol., July 1941, 3 pp.
24. SCHEUTTE, C. N. Quicksilver. Bureau of Mines Bull. 335, 1931, 168 pp.
25. _____. Quicksilver. Modern Uses of Nonferrous Metals. AIME, 2d ed., 1953, pp. 318-332.

26. SEGURA, D. AIME Tech. Pub. 896, Metals Technol., February 1938, 7 pp.
27. SHAFFER, L. H., NEWTON, J., and FAHRENWALD, A. W. Flotation of Mercury Ores. Eng. and Min. Jour., May 1940, p. 40.
28. SMITH, P. S., and MADDREN, A. G. Quicksilver Deposits of the Kuskokwim Region. Geol. Survey Bull. 622-H, 1915, pp. 272-291.
29. SPURR, J. E. A Reconnaissance in Southwestern Alaska in 1898. Geol. Survey 20th Ann. Rept., Pt. 7, 1900, p. 261.
30. SPURR, J. E., and POST, W. S. Report of the Kuskokwim Expedition-Maps and Descriptions of Routes of Exploration in Alaska in 1898. Geol. Survey, 1899.
31. SWINEFORD, A. P. Report of the Governor of Alaska for the Fiscal Year 1886-1886, p. 949.
32. _____. Report of the Governor of Alaska for the Fiscal Year 1888-1888, p. 18.
33. TAGGART, A. F. Handbook of Mineral Dressing. John Wiley & Sons, Inc., 1945, pp. 2-206 - 2-209.
34. THORNHILL, E. B. Recovery of Mercury From Amalgamation Tailing. AIME Bull. 104, 1915.
35. TREADWELL, F. P., and HALL, W. T. Analytical Chemistry. John Wiley & Sons, Inc., vol. I, 9th ed., 1949, p. 119.
36. VAN ARSDALE, G. D. Hydrometallurgy of Base Metals. McGraw-Hill Book Co., Inc., 1953, p. 29.
37. VON BERNEWITZ, M. W. Occurrence and Treatment of Mercury Ore at Small Mines. Bureau of Mines Inf. Circ. 6966, 1937, 40 pp.
38. WALLACE, R. E. Preliminary Report on the Quicksilver-Antimony Properties in the Vicinity of Sleitmute, Georgetown District, Southwestern Alaska. Geol. Survey, 1943.
39. WEBBER, E. J., and HOARE, J. M. Quicksilver-Antimony Deposits Near DeCoursey Mountain, Iditarod District, Southwestern Alaska. Geol. Survey unpublished report, December 1943.
40. WEBBER, B. S., BJORKLUND, S. C., RUTLEDGE, F. A., THOMAS, B. I., and WRIGHT, W. S. Mercury Deposits of Southwestern Alaska. Bureau of Mines Rept. of Investigations 4065, 1947, 57 pp.
41. WELLS, R. R. Laboratory Concentration of Mercury Ores From Oregon, California, Idaho, and Nevada. Bureau of Mines Rept. of Investigations 4620, 1950, 19 pp.
42. FEDERAL GEOLOGICAL SURVEY. Mineral Resources of the United States, 1882-1923.
43. FEDERAL BUREAU OF MINES. Mineral Resources of the United States, 1924-31; Minerals Yearbook, 1932-53.