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Recovering Zinc-Lead Sulfide From a Geothermal Brine

By L. E. Schultze and D. J. Bauer



UNITED STATES DEPARTMENT OF THE INTERIOR



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UNITED STATES DEPARTMENT OF THE INTERIOR
William P. Clark, Secretary

BUREAU OF MINES
Robert C. Horton, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb/h	pound per hour
cm/min	centimeter per minute	mg/L	milligram per liter
d/yr	day per year	min	minute
ft/h	foot per hour	mL	milliliter
ft ²	square foot	mm	millimeter
g	gram	μm	micrometer
(gal/ft ²)/h	gallon per square foot per hour	MW	megawatt
g/L	gram per liter	pct	percent
h	hour	ppm	part per million
in	inch	psig	pound per square inch, gauge
L	liter	ton/d	ton per day
lb	pound	ton/yr	ton per year
(lb/ft ²)/h	pound per square foot per hour		

RECOVERING ZINC-LEAD SULFIDE FROM A GEOTHERMAL BRINE

By L. E. Schultze¹ and D. J. Bauer²

ABSTRACT

The Bureau of Mines devised a technique to recover a Zn-Pb concentrate from a geothermal brine. More than 99 pct of the Zn and Pb was precipitated by treating the brine with H₂S and controlling the pH with lime. Recycle of the sulfide precipitates increased crystal size and resulted in easily filterable products. A typical sulfide precipitate contained 53 pct ZnS, 8 pct PbS, 24 pct MnS, and 15 pct FeS. Addition of sulfide as FeS or CaS was not effective in precipitating Zn and Pb, but Zn in the brine was selectively removed with a strongly basic ion-exchange resin. A proposed flowsheet for metals recovery is discussed.

¹Research chemist.

²Supervisory chemical engineer.

Reno Research Center, Bureau of Mines, Reno, NV.

INTRODUCTION

While geothermal brines have been extensively investigated, most efforts have concentrated on energy recovery. Little attention has been given to metal salts contained in the brines, and only their effects on corrosion, scaling, or plugging of the wells have been addressed. Some geothermal reservoirs, particularly those in the Imperial Valley of California, contain significant quantities of valuable metals and represent large, low-grade resources.

The Bureau of Mines has investigated the recovery of these metals, as well as funding several contract studies in this area. One of the studies proposed an industrial complex to make higher value products from components of the brine (1).³ Other contract studies concentrated on recovering metal values from brine that was returned to injection wells after the heat had been removed in the form of steam for electrical power generation. After steam removal, the brine streams are referred to as post-flash brine. Metals recovery from post-flash brine would not interfere with energy recovery.

In one of the studies, postflash brine was treated with lime to increase the pH from 5.5 to 8.5 and precipitate Fe, Mn, Pb, and Zn (2). An engineering design was completed (3), and a mineral recovery unit was assembled and operated (4). Data from the mineral recovery unit demonstrated that more than 95 pct of the Fe, Mn, Pb, and Zn could be recovered as a precipitate containing 50 to 60 pct water, 20 to 25 pct soluble chlorides, and 15 to 20 pct mixed hydrous oxides. No satisfactory method was found to separate the contained metal values.

Another contract study demonstrated that Li could be precipitated from brines by adding a solution of $AlCl_3$ and increasing the pH to 7.5 with lime (5). Treatment of the hydrous Al-Li oxide precipitate was investigated, and techniques were devised to recover a LiCl product (6). Treatment steps included separation of Li and Al and recovery of Al as a chloride salt suitable for recycle to the Li precipitation step. LiCl was concentrated and purified to yield a 99.9-pct-pure product. Overall Li recovery from the brine was 89 pct.

A method for recovering a Zn-Pb sulfide concentrate from a geothermal brine was also demonstrated (7) and is described in the "Background" section of this report. Two problems were observed: the cost of the Na_2S reagent and poor solid-liquid separation of the sulfide precipitate.

Successful resolution of the economic and technical problems in precipitating Zn and Pb sulfides would make a significant zinc resource available. Estimates for power generation from the brines of the Imperial Valley are that 1,600 to 5,200 MW will be produced by the year 2000 (8). Using estimates of 7.5×10^6 lb/h of postflash brine for 100 MW of power generation and the minimum power projection of 1,600 MW, and assuming the brine contained an average of 240 ppm of Zn, 90 pct recovery for 300 d/yr of operation would provide more than 90,000 ton/yr Zn. Annual domestic consumption of zinc for 1981 was 1,300,000 tons and included imports of 790,000 tons (9).

This report discusses evaluations of less expensive reagents for sulfide precipitation and techniques to increase the grain size of the sulfides so that precipitate filtration and washing characteristics are improved. A flowsheet is included and combines several metals recovery techniques into a proposed overall treatment method.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

BACKGROUND

Conditions for precipitation of metal sulfides from geothermal brine were evaluated by SRI International during a contract study (7). Investigations were made on brines obtained from the Salton Sea Known Geothermal Resource Area in the Imperial Valley of California. Brines from three wells, Elmore No. 2, Magmamax No. 1, and Woolsey, located near the southern end of the Salton Sea (fig. 1) were used. The brines were similar in composition but contained different concentrations of the metals (table 1). The variations in composition are similar to those found in brines from a single well at different flow rates (10). Composition of brines is dependent on flow rate, temperature, pressure, and pH. Therefore, different compositions may be

reported for wells drawing from the same reservoir.

TABLE 1. - Average analyses of geothermal brines, milligrams per liter

	Elmore No. 2	Magmamax No. 1	Woolsey
Na..	70,000	58,000	38,000
Ca..	33,000	25,000	19,000
K...	21,000	12,000	8,800
Mn..	1,700	680	470
Fe..	840	190	170
Ba..	610	115	140
Sr..	530	520	330
Zn..	460	270	120
B...	390	250	220
Li..	240	170	120
Mg..	80	84	150
Pb..	49	49	40
SiO ₂	NA	230	84

NA Not available.

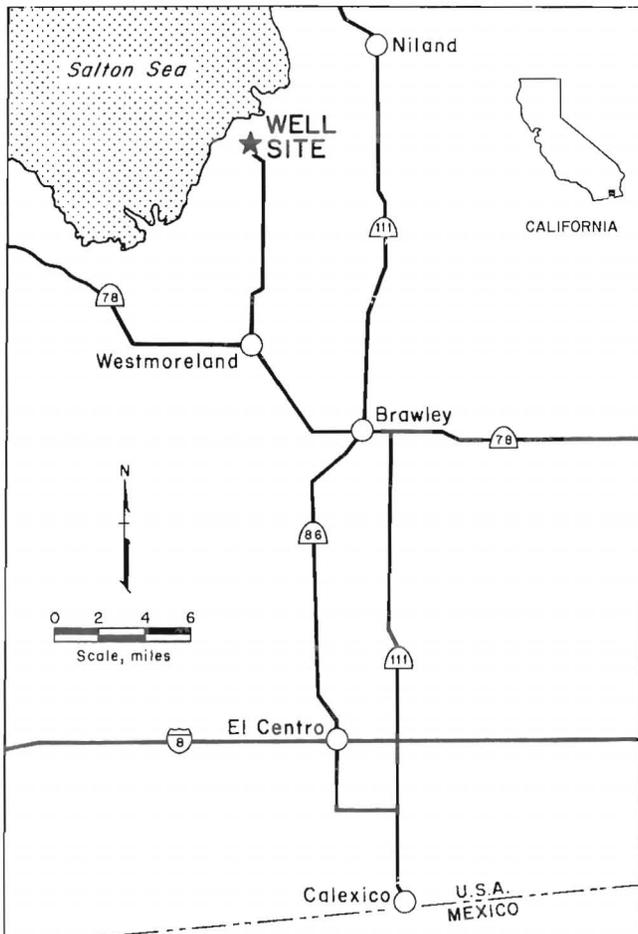


FIGURE 1. - Location of well site.

Figure 2 shows the effects of pH and sulfide concentration on the precipitation of metals. The sulfide concentration is expressed as the stoichiometric ratio of sulfide to total Zn and Pb. At pH 3.5 and a Na₂S mol ratio of 3:1, 95 pct of the Zn and 90 pct of the Pb were precipitated while 80 pct of the Fe and 95 pct of the Mn remained in solution. Lower sulfide additions were effective for PbS precipitation but resulted in poor ZnS precipitation unless higher pH's were used. When the pH was increased, greater amounts of FeS were precipitated with each sulfide addition. At stoichiometric ratios of less than 2 sulfide to total Zn and Pb and up to pH 4.0, which was the highest pH used, more than 80 pct of the Fe remained in solution.

The use of H₂S for metals precipitation was also studied; however, this required that a base be added to neutralize acid liberated by the precipitation reaction. Using Na₂S instead of H₂S alleviated the problem of acid liberation and eliminated the need to add a base; this was the method of choice in the contract study. When the brine was treated with a solution of Na₂S equivalent to 1.6 times the

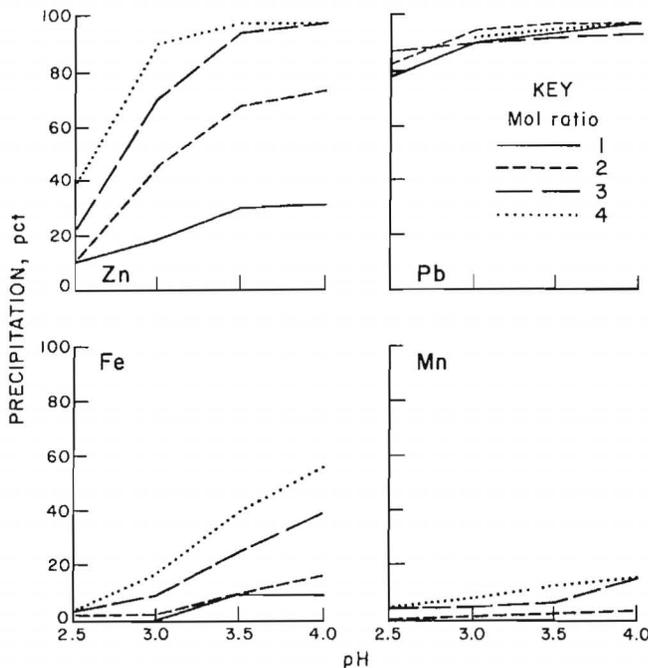


FIGURE 2. - Percent precipitation of metals from Woolsey brine at increasing mol ratios of Na₂S to total Zn and Pb versus pH, at 90°C.

stoichiometric requirement for Zn and Pb, pH values of 4.8 to 5.2 were obtained. Results showed that 79 to 92 pct of the Zn, 72 to 92 pct of the Pb, 31 to 46 pct of the Fe, and 18 to 25 pct of the Mn were precipitated. The main difference among the tests was that the brine was pretreated with Fe filings prior to the sulfide addition in the test having a final pH of 5.2. The purpose of adding the Fe filings was to reduce the Fe in solution to ferrous ion so that approximate postflash brines were obtained. Aging of the brine caused some of the Fe to oxidize. Since sulfide ion is reduced to S in the presence of ferric ions, reduction of the Fe minimized consumption of Na₂S. Treatment of the brine with Fe filings was observed to increase Fe concentration by 35 pct and to remove 70 pct of the Pb by cementation but also to yield the highest percent precipitation of Zn and Fe. The precipitation differences were not large and suggest that most of the ferric ion had precipitated as hydrous Fe₂O₃ prior to withdrawing the test samples.

The contract study also evaluated settling, filtration, and washing of the sulfide precipitates obtained by adding Na₂S at a stoichiometric ratio of 1.6. The sulfides formed 1- to 2-mm floccules without the aid of a flocculating agent. The floccules settled rapidly to 0.7 pct solids (fig. 3). Recycle of precipitated sulfides to increase the initial solids from 0.08 to 0.20 pct did not improve the settling rate, but an initial percent solids of 1.0 yielded a settled pulp of 1.4 pct solids, which represents a decrease in thickener requirements. Thickener requirements for a feed rate of 1 ton/d solids and an underflow of 2.3 pct solids were 117 ft² for a feed slurry containing 0.08 pct solids, 119 ft² for 0.20 pct solids, and 88 ft² for 1.00 pct solids. The thickener requirements for the sulfide slurries would be large even if precipitate recycle were employed.

Filtration tests showed that the sulfide precipitates were difficult to filter. Filtration in a 6-in pressure filter using Whatman No. 14 filter paper increased the solids from 2.3 to 23 pct. Filtration rates were slow, and increased

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

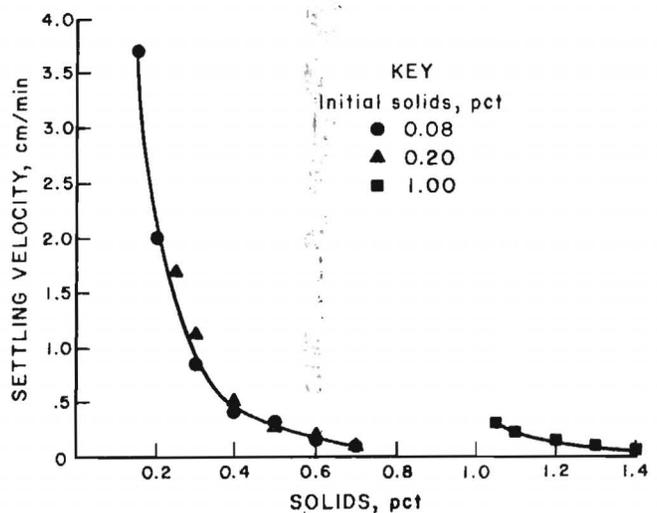


FIGURE 3. - Settling velocity as a function of percent solids.

pressure was marginally beneficial (fig. 4). Filtration at a constant pressure difference of 30 psig required 28 min for a 1/2-L sample. Increasing the pressure to 60 psig decreased filtration time to approximately 19 min, which represents a filtration rate of 1.7 (gal/ft²)/h. The filter cake was washed free of entrained brine by a 1-volume displacement wash. The FeS and MnS in the washed filter cakes were amorphous, while ZnS and PbS were fine-grained crystals. X-ray diffraction patterns showed that PbS grains were 0.15 μm in size and ZnS grains measured 0.01 μm . The washed and dried precipitate contained 31 pct ZnS, 5 pct PbS, 14 pct MnS, 9 pct FeS, and 41 pct acid insolubles, which were mostly silica.

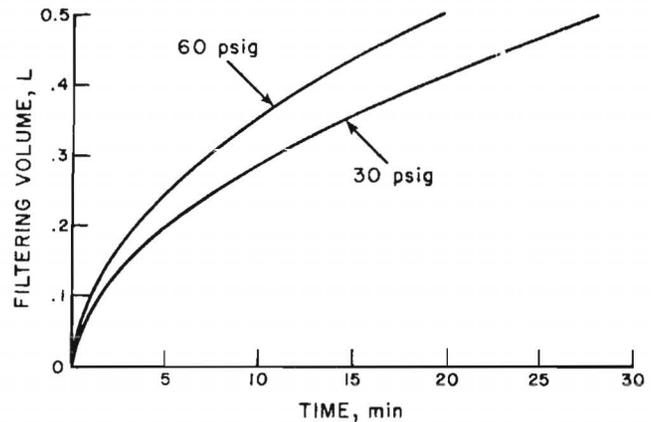


FIGURE 4. - Filtrate volume versus time during pressure filtering of 2.3-pct-solids feed slurry.

MATERIALS AND PROCEDURES

In-house investigations used brines from the same wells employed by the contract study (7). Standard bench-scale equipment and reagent-grade chemicals were used, except as specified in the "Results and Discussion" section. Solutions were analyzed by inductively

coupled plasma. Solid samples were dissolved in a known volume of acid and analyzed as solutions. Additions of H₂S gas were measured by loading a 150-mL bomb to 6 psig and weighing the bomb before and after the tests.

RESULTS AND DISCUSSION

SULFIDE PRECIPITATION

Since the contract study indicated that good separation of Zn and Pb from Fe and Mn and good recovery of Zn and Pb could be achieved with sulfide additions of 3 to 4 times the stoichiometric ratio for Pb and Zn and at a pH of 3.5 (fig. 2), a test was made using 3.5 times the stoichiometric ratio of Na₂S at pH 3.5. The precipitated sulfides were compared with precipitates obtained at pH 5.2 and a sulfide addition of 1.6 times the stoichiometric ratio for total Zn and Pb. Composition of the metal sulfides (table 2) showed that the concentration of Zn increased at the lower pH while Fe and Mn decreased. The lower value for Pb at the lower pH may be because the Pb was present at concentrations close to its detection limit.

Subsequent efforts concentrated on improving the solid-liquid separation characteristics by increasing the grain size of the Zn-Pb sulfides. Two techniques, use of a sulfide reagent that would react more slowly, such as FeS, and recycle of sulfide precipitate to act as seed, were considered. FeS has been used in treating waste streams to remove contaminants that form less soluble sulfides (11). Recycle of sulfide precipitates improved sulfide precipitation characteristics of Cu (12).

TABLE 2. - Comparison of metal sulfide precipitate compositions

Sulfide addition, mol ratio	pH	Metal sulfides, pct			
		ZnS	MnS	FeS	PbS
1.6	5.2	53	24	15	8
3.5	3.5	69	17	10	4

In tests using reagent-grade FeS, pyrrhotite, and pyrite at pH 3.5, only 10 pct of the Zn was precipitated from the brine. A freshly prepared sample of FeS was obtained by treating a brine sample with Na₂S to precipitate ZnS and PbS, which were removed by filtration, and then again with Na₂S to precipitate FeS and MnS. The Fe-Mn sulfides were added to a fresh brine sample at 80° C to precipitate PbS and ZnS. After 2 h of contact at pH 3.5, 88 pct of the Pb and 39 pct of the Zn were precipitated.

Since precipitation of Zn was incomplete with FeS, tests were run with a commercial reagent containing 72 pct CaS. Good results were reported (13) in treating waste streams with CaS to obtain easily filterable metal sulfides. Tests at pH 3.5 and 25° C showed that on a molar basis, more CaS was required than Na₂S (fig. 5). A repeat of the tests 3 weeks later demonstrated that the reagent was unstable and the percent of metals left in solution at a given addition rate was higher. Even though precipitation results similar to those obtained with Na₂S were obtained at 90° C, the unstable nature of the reagent made reproducible results difficult to obtain and no further work was done with CaS.

Because FeS reacted too slowly with the brine and CaS was not stable, tests were

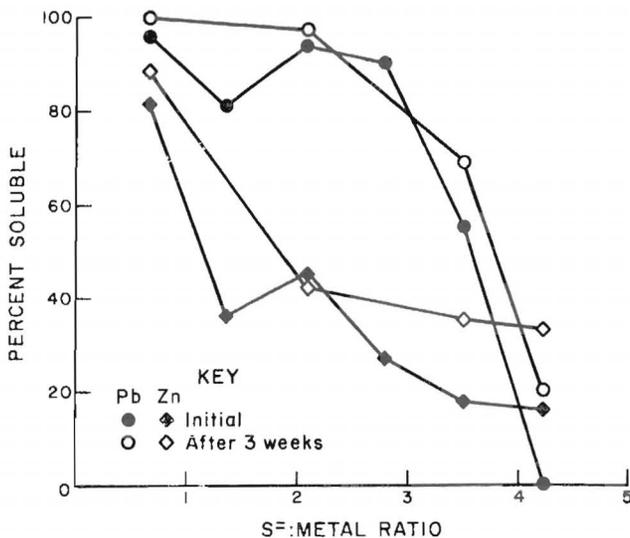


FIGURE 5. - Precipitation of Zn and Pb by CaS.

made using H₂S with lime to control the pH. More than 99 pct of the Zn and Pb was precipitated from the brine at a pH of 3.5, with sulfide addition equal to 3.5 times the stoichiometric ratio for Zn and Pb, and at 89° to 98° C. Tests were run in a 2-L resin kettle with mechanical stirring, and pH was controlled by adding 20 pct lime slurry. When the requisite quantity of H₂S was added (0.9 g for a 1-L test) and the pH was stabilized, the reaction slurries were filtered and the filter cake was added to a fresh batch of brine. Five cycles of sulfide precipitation were completed, with recycle of half of the filter cake for cycles 2 to 4. The unused portion of the filter cakes was analyzed by scanning electron microscopy (SEM). The SEM photographs of precipitates from cycles 2 and 5 showed that sulfide particles increased from less than a micrometer to 1 to 3 μm in size (fig. 6). Elemental analyses of specific sites, A through E, in the precipitates showed that all three sites in the cycle 2 precipitate were mixtures of FeS, ZnS, and PbS. The non-crystalline site, D, in the cycle 5 precipitate was mostly FeS, while the crystalline particle, site E, was a mixture of ZnS and PbS containing a lower percentage of FeS. A similar result was reported for the recycle technique applied to precipitation of CuS (12). Burnham and Sumner reported an increase from 0.05 to 0.25 to ~25 μm. The larger CuS particles increased settling rates from 0.43 to 0.76 ft/h and filtration rates from 0.35 to 1.36 to 4.32 (lb/ft²)/h. Similar improvements for the Zn-Pb sulfide precipitates obtained from brines would mitigate the solid-liquid separation problem reported for treatment using Na₂S (7).

MAGNESIUM AND IRON PRECIPITATION

Having demonstrated techniques for improved precipitation of a Zn-Pb sulfide fraction, consideration was given to removing the remaining Fe and Mn. Precipitation of Fe and Mn would result in another potential byproduct and should remove residual sulfide from the brine.

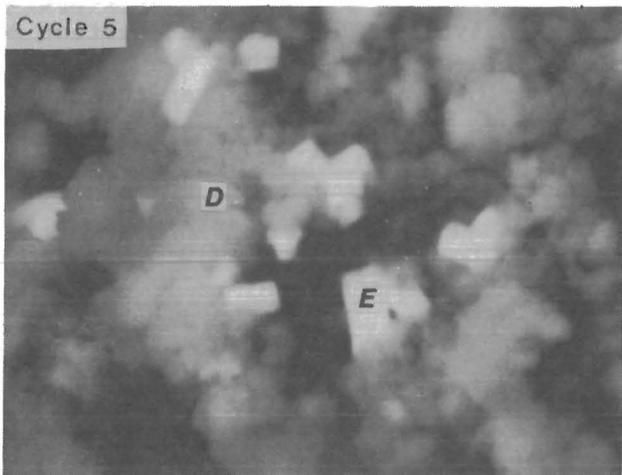
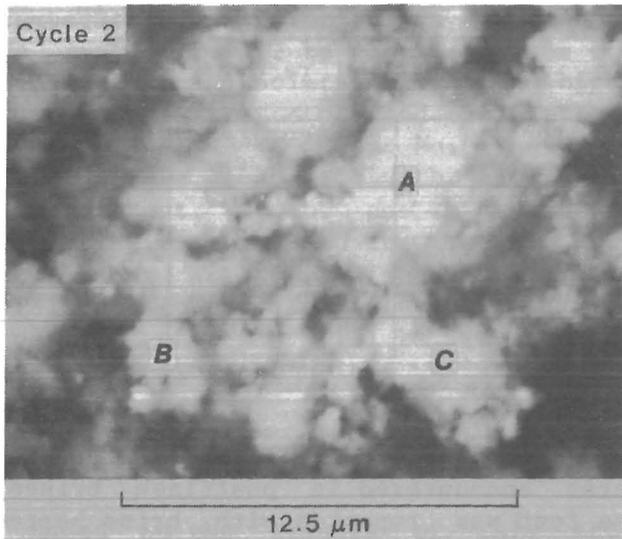


FIGURE 6. - SEM photographs of sulfide precipitates.

A brine from Elmore No. 2 was treated with 3.5 times the stoichiometric ratio of Na_2S at pH 3.6 and 90°C . The sulfide precipitate was removed by filtration, and the filtrate pH was adjusted to 8.5 with a 20 pct slurry of $\text{Ca}(\text{OH})_2$. The hydroxide precipitate that formed was filtered, reslurried in water, filtered again, and washed. Filtrates, wash solution, and the washed hydroxide precipitate were analyzed. A portion of the precipitate was calcined at 850°C and examined by SEM. The remainder was dissolved in HCl and analyzed by inductively coupled plasma.

Analyses of the filtrates from precipitation (table 3) showed that most of the

Zn and Pb were removed by sulfide treatment and Fe and Mn were precipitated by the $\text{Ca}(\text{OH})_2$ addition. The majority of the Mg was precipitated as a hydroxide, but other metals remained in solution. Analyses of the wash solutions, given in table 4, showed good removal of Na while K and Ca removal was less effective.

TABLE 3. - Precipitation of metal values, percent

Treatment	Fe	Mg	Mn	Pb	Zn
Sulfide.....	35	11	22	>68	88
Hydroxide.....	65	73	78	ND	11

ND Not detected.

TABLE 4. - Distribution of soluble chloride salts during washing, percent

	Ca	K	Na
Repulp wash.....	82.3	87.0	92.9
Displacement wash.....	7.3	5.0	6.7
Washed filter cake....	10.4	8.0	.4

Analyses of the brine filtrate after the two precipitation steps showed the presence of S species in solution even though the $\text{Ca}(\text{OH})_2$ treatment was expected to remove residual sulfide. The filtrate contained 0.35 g/L sulfate and 0.11 g/L sulfide. The presence of sulfate would explain the poor washing of Ca. The Ca concentration in the displacement wash was consistent with the solubility product for CaSO_4 . The Ba and Sr concentrations in the filtrate were also analyzed to check for sulfate. The concentrations of both had decreased to levels consistent with the presence of the sulfate.

A mass balance for S was calculated assuming that Fe, Mn, Pb, and Zn were precipitated as sulfides during addition of Na_2S and that Ba and Sr were precipitated as sulfates. Closure for total S was 103 pct. These calculations indicated that no S^- was precipitated during the treatment with $\text{Ca}(\text{OH})_2$.

The precipitate from the $\text{Ca}(\text{OH})_2$ treatment gave a Mn-Fe concentrate that could be calcined to a fine-grained oxide. SEM photographs of the calcined precipitate

showed that individual grains of 1 μm or less had agglomerated into groupings of 20 to 30 μm . The major metals identified were Mn, Fe, and Ca. An approximate composition of the dried precipitate was calculated based on the metals analyses and the most probable metal species present (table 5).

TABLE 5. - Composition of precipitate obtained by treatment with $\text{Ca}(\text{OH})_2$, percent

$\text{Al}(\text{OH})_3$	1.4	$\text{Mg}(\text{OH})_2$	6.6
CaSO_4	12.7	MnO_2	54.0
$\text{Cr}(\text{OH})_2$3	$\text{Ni}(\text{OH})_2$3
Fe_2O_3	19.5	$\text{Zn}(\text{OH})_2$	3.1
KCl	2.1		

ZINC SEPARATION BY ION EXCHANGE

During research on the geothermal brines, an alternative method for separating Zn from other constituents of the brine was considered. Since Zn was present as an anionic chloride complex, it could be removed by using a strong base anion-exchange resin. Iron would extract with the Zn if the Fe was oxidized to the trivalent state but would be rejected if it was present as the divalent ion. The majority of the Fe in postflash brines would be reduced and would remain in the brine. Tests were run in which the brine sample was treated with Fe filings to reduce the Fe^{3+} in solution. The treated brine was passed through a column containing a strong base ion-exchange resin. The loaded resin was washed with a 25-pct- NaCl solution and stripped with water. In a test at ambient temperature, more than 99 pct of the Zn in a 100-mL sample of Elmore No. 2 brine was adsorbed on 8 g of AG-1-X2 resin, which contained 70 to 76 pct water. Less than 0.4 pct of the loaded Zn was removed by washing with 50 mL of the 25-pct NaCl . The stripping solution was collected in 10-mL fractions and analyzed for distribution of the metals (table 6). Lithium and lead were not detected in the stripping solutions, and small quantities of Mn (<1 ppm) were in each fraction. The combined stripping solution contained 89.7 pct Zn, 10.3 pct Fe, and less than 0.05 pct Mn.

TABLE 6. - Water-stripping of Zn and Fe from AG-1-X2 exchange resin, percent recovery

Stripping volume, mL	Ambient temp		85°-95° C	
	Zn	Fe	Zn	Fe
0-10.....	0.1	0.7	1.6	0
10-20.....	59.5	98.9	30.6	100
20-30.....	39.6	.4	55.0	0
30-40.....	.6	0	12.8	0
40-50.....	.1	0	0	0
50-60.....	.1	0	ND	ND

ND Not detected.

To determine the effect of the temperatures encountered in postflash brines, the test was repeated with brine heated to 85° to 95° C. Adsorption of Zn from 100 mL of brine was 94.4 pct compared with more than 99 pct at ambient temperature. Analysis of each 10-mL fraction of brine effluent showed that the resin approached loaded conditions at the higher temperature but not under ambient conditions. At 85° to 95° C, no Zn was detected in the 1st two fractions, but 2 pct remained in the 3d fraction, and this increased to 12 pct in the 10th fraction. At ambient temperature, all 10 fractions contained less than 1 pct of the Zn. Further evidence that the resin was near loading capacity at the higher temperature was that 9 pct of the Zn was removed by washing with 25-pct- NaCl solution compared with 0.4 pct in the ambient temperature test. Zinc was detected in equal amounts in each of the five fractions of 25-pct- NaCl washing solution. Entrained brine from the loading sequence was removed by the first two fractions of washing solution as evidenced by Li and Mn analyses. The net result was that loaded, washed resin removed 86 pct of the Zn from postflash brine at 85° to 95° C compared with 99 pct at ambient temperature.

Stripping of the resin with water was complete after 40 mL had exited the column (table 6). The Zn was concentrated in the second and third fractions of the ambient test but was present in significant quantities in each of the four fractions from the test at higher temperature. As was the case at ambient

temperature, no Li or Pb was detected but Mn ranged from 2 to 30 mg/L. The combined stripping solution from the higher temperature test contained 94.4 pct Zn, 4.8 pct Fe, and 0.8 pct Mn. The lower level of Fe, compared with that in the ambient test, may be due to hydrolysis and precipitation on the resin. While operation at the higher temperature yielded a purer Zn solution, a larger quantity of resin will be required and the stripping solution will be more dilute.

PROPOSED COMBINATION FLOWSHEET

Based on the results of this study and previous reports on metals recovery from geothermal brines (4, 6), a metals

SUMMARY AND CONCLUSIONS

Results of the contract study (7) demonstrated that ZnS and PbS were precipitated from a geothermal brine in preference to FeS and MnS. The precipitation technique used expensive Na_2S and resulted in a low-percent-solids product that was difficult to filter. Improvements were achieved by replacing Na_2S with H_2S and lime and recycling part of the precipitated sulfides. The less costly reagents yielded larger sulfide particles that settled and filtered more easily. An alternative recovery scheme involving ion exchange was demonstrated. An anionic ion-exchange resin selectively removed Zn when Fe was in the divalent state.

Evaluation of residual sulfide from the precipitation step indicated the presence of sulfate in the treated brine. Generation of sulfate would not be expected in the reducing conditions present in fresh postflash brines, but its presence should be monitored because it would cause precipitation within the injection well.

Recovery of a Mn-Fe oxide fraction was also demonstrated. The oxide was fine

recovery flowsheet (fig. 7) is proposed. Removal of silica would be beneficial to avoid contamination of byproduct streams. Silica removal is routinely practiced during power generation to avoid plugging of injection wells.

Sulfide treatment would yield a Zn-Pb sulfide product similar to flotation concentrates from commercial ores. The ion-exchange alternative would yield a solution of ZnCl_2 . Lime treatment would yield a Mn-Fe oxide. If the ion-exchange alternative for Zn recovery is used, the Mn-Fe oxide would contain approximately 1 pct PbO since Pb is not removed by ion exchange. Lithium recovery would yield a LiCl product comparable to those marketed by current domestic producers (6).

grained and contained some CaSO_4 , KCl , and $\text{Mg}(\text{OH})_2$. While the oxide would not be suitable for use in steel or batteries without purification, it may be suitable as a neutralizing agent or for stack gas scrubbing.

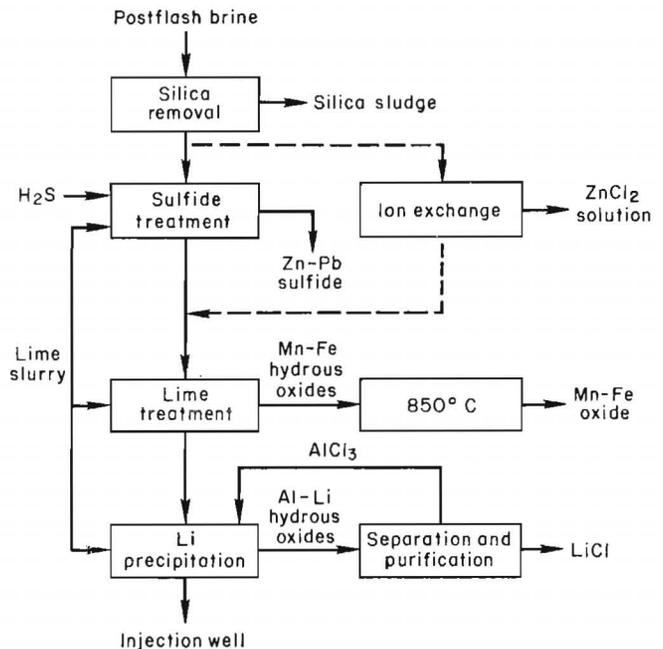


FIGURE 7. - Combination metals recovery flowsheet.

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