BuMines OFR 81-75

PB-245 686

HAZEN RESEARCH, INC.

4601 INDIANA STREET
GOLDEN, COLORADO • 80401
TELEPHONE 303/279-4501

HRI Project 1370-01

THE RECOVERY AND SEPARATION OF MINERAL VALUES FROM GEOTHERMAL BRINES

for

U. S. Department of Interior
Bureau of Mines
Washington, D. C. 20240

Bureau of Mines Open File Report 81-75

June 12, 1975

Approved by:

C. E. Berthold

C. E. Berthold
Senior Research Engineer

F. M. Stephens, Jr.
Executive Vice President

BIBLIOGRAPHIC DATA SHEET	1. Report No. BuMines OFR 81-75	2.	3. Recipient's Accession No.

4. Title and Subtitle

The Recovery and Separation of Mineral Values From Geothermal Brines

5. Report Date June 12, 1975

6. Performing Organization Code

7. Author(s)
D. H. Christopher, Maxine Stewart, and Janet Rice

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Hazen Research, Inc.
4601 Indiana Street
Golden, Colorado 80401

10. Project/Task/Work Unit No.

11. Contract/~~Grant~~ No. H0144104

12. Sponsoring Agency Name and Address
Office of Assistant Director - Metallurgy
Bureau of Mines
U. S. Department of the Interior
Washington, D. C. 20241

13. Type of Report & Period Covered Contract research, 1974-75.

14. Sponsoring Agency Code

15. Supplementary Notes
Approved for release by Director, Bureau of Mines, September 22, 1975.

16. Abstracts The subject laboratory process study on recovery and separation of minerals from Sinclair No. 4 geothermal brines developed methods for recovering iron and manganese hydrated oxide compounds as separate components essentially quantitatively. In addition, lead and zinc values were also removed, essentially quantitatively, as co-precipitated compounds together with the hydrated manganese oxides. Processes were developed for the recovery of iron, manganese, zinc, lead, barium, lithium, and ammonia values from the brine. Greater than 99 percent of the total heavy metal values were separated at pH ≈ 8.7 under nonoxidizing conditions using lime as a precipitant. As an alternative, iron may be selectively precipitated as a hydrated magnetic oxide at pH ≈ 6.0, again using lime as precipitant, but under controlled air oxidation. The remaining heavy metals were subsequently brought down with lime under oxidizing alkaline conditions. Iron was recovered as a magnetic oxide product containing 68 percent Fe, manganese, zinc, and lead as a mixed oxide product containing 47.3 pct Mn, 18.2 pct Zn, and 2.8 pct Pb.

17. Key Words and Document Analysis. 17a. Descriptors

Geothermal brines
  Recovery of mineral values
    Iron
    Manganese
    Zinc
    Lead
    Barium
    Lithium
    Ammonia values

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 11F

i

18. Distribution Statement Release unlimited by NTIS.	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages
	20. Security Class (This Page) UNCLASSIFIED	

Notice:

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies or recommendations of the Interior Department's Bureau of Mines or of the U. S. Government.

TABLE OF CONTENTS

FOREWORD

This report was prepared by Hazen Research, Inc., under U. S. Bureau of Mines Contract No. HO144104. The contract was initiated under the Bureau of Mines Metallurgy Program. It was administered under the technical direction of Metallurgy, with Mr. Don H. Baker, Jr., acting as the Technical Project Officer. Mr. W. L. Miller was the contract administrator for the Bureau of Mines.

This report is a summary of the work recently completed on this contract during July, 1974, to February, 1975. This report was submitted by the authors on May 28, 1975.

We would like to acknowledge the guidance and assistance of Mr. Don H. Baker, Jr., throughtout the course of the subject investigation, and Mr. W. C. McCulloch, Chief Geologist, Southern Pacific Land Company, for assistance in obtaining samples of Sinclair No. 4 brine.

This report was prepared by the following Hazen Research, Inc. employees:

D. H. Christopher, Senior Analyst
Maxine Stewart, Analyst
Janet Rice, Technician

ABSTRACT

The subject laboratory process study on recovery and separation of minerals from Sinclair No. 4 geothermal brines developed methods for recovering iron and manganese hydrated oxide compounds as separate components essentially quantitatively. In addition, lead and zinc values were also removed, essentially quantitatively, as co-precipitated compounds together with the hydrated manganese oxides.

The hydrated iron oxides were converted into a magnetic iron oxide product containing in excess of 68% iron, and less than 0.1% Mn, thus enabling its essentially complete separation from the manganese, lead, and zinc compounds.

Manganese was recovered as a hydrated oxide product, together with co-precipitated lead and zinc values, and contained 47.3% manganese, 18.2% zinc, and 2.8% lead with 0.6% iron contamination.

Lithium was recovered as the aluminate in yields greater than 99% at a grade of 8.0% Li_2O for a concentration factor of 320, relative to the lithium level in the starting Sinclair No. 4 brine, using a much lower Al/Li ratio than was heretofore believed possible.

Sufficient design data were obtained during the course of this investigation to enable construction of a pilot scale demonstration plant for the recovery of mineral values from Sinclair No. 4 brine should this be desired.

Exploratory tests indicated that of the alkaline earth metals present, only barium can be easily recovered from the pre- or post-flash brine by precipitation with sodium sulfate. Recovery of strontium values by sulfate precipitation is feasible only if the Sinclair No. 4 geothermal fluid can be concentrated two to three-fold, basis the original input fluid.

INTRODUCTION AND SUMMARY

During July, 1974, Hazen Research, Inc., undertook a program of work under the sponsorship of the United States Bureau of Mines (Contract HO144104) to determine methods for recovery of mineral values from geothermal brines. The experimental program was completed in February, 1975, and this report summarizes the work done and results obtained.

Wellhead brine, both pre-flash and post-flash, from the Sinclair No. 4 well, Imperial Valley, California was chosen for the study. Processes have been developed for the recovery of iron, manganese, zinc, lead, barium, lithium, and ammonia values from the brine. Greater than 99% of the total heavy metal values were separated at pH = 8.7 under nonoxidizing conditions using lime as a precipitant. As an alternative, iron may be slectively precipitated as a hydrated magnetic oxide at pH = 6.0, again using lime as precipitant, but under controlled air oxidation. The remaining heavy metals were subsequently brought down with lime under oxidizing alkaline conditions. Iron was recovered as a magnetic oxide product containing 68% Fe, manganese, zinc, and lead as a mixed oxide product containing 47.3% Mn, 18.2% Zn, and 2.8% Pb.

Lithium was separated by precipitation with aluminum hydroxide at pH = 7.5. Recoveries of greater than 99% were obtained.

Experimental data show that 90% of the total barium content of the brine can be precipitated using sodium sulfate. With controlled excess of precipitant, 75% of the barium content can be precipitated free of strontium.

COMPOSITION OF BRINE

Table 1 shows a typical analysis of the Sinclair No. 4 "post-flashed" brine. The data are a composite of analyses obtained by mass spectroscopic and wet chemical methods.

The wellhead brine was found to be totally reduced with respect to iron and manganese, hence very susceptible to atmospheric oxidation. Accordingly, the working samples were flashed at the wellhead under anaerobic conditions and were stored in sealed containers under nitrogen for the duration of the test program.

Table 1

Typical Composition of Sinclair No. 4 Brine

Element	ppm	Element	ppm	Element	ppm	Element	ppm
Ag	0.5	Ce	10	Mn	2000	Se	2.5
Al	0.6	Cu	0.5	Mo	10	Si	40
As	3.	F	10	Na	70,000	SO_4	0.04
B	400	Fe	1200	Nb	0.1	Sr	600
Ba	200	Ga	0.5	NH_4	650	Ta	6
Br	200	Ge	1.	Ni	0.5	Ti	2.5
Ca	35,000	I	0.5	P	0.5	V	0.3
Cd	0.9	K	19,000	Pb	100	Zn	500
Cl	190,000	Li	250	Rb	25	Zr	8
Cr	2	Mg	150	S	0.1		

It will be noted that the silica content of the Sinclair No. 4 brine samples used averaged only 40 ppm, as contrasted to the normal value of 750 ppm obtained from fresh wellhead brine. Most of the dissolved silica in the brine precipitates upon cooling and standing so that the material used for the herein described test work was not truly representative of fresh wellhead brine.

In order to operate upon a truly representative wellhead brine sample, it would be necessary to construct an on-site pilot demonstration plant for the purpose.

REMOVAL OF TOTAL HEAVY METALS BY PRECIPITATION

The major heavy metals contaminants in Sinclair No. 4 brine are manganese, iron, zinc, and lead (Table 1). Manganese, iron, and zinc form insoluble hydroxides according to Table 2. Precipitation of these metals from aqueous solutions is essentially complete within the pH range 8.5-9.0 (1,2). The hydroxide of lead is sparingly soluble (0.155 g/l) in neutral aqueous solution.

Table 2

Solubility Products of Heavy Metal Hydroxides 1/

Species	Ksp (°C)	Approximate pH Range
Ferrous hydroxide	1.6×10^{-14} (18)	>6.5
Ferric hydroxide	1.1×10^{-36} (18)	>2.5
Manganese (II) hydroxide	4×10^{-14} (18)	>8.5
Zinc hydroxide	1.8×10^{-14} (18-20)	6.5-9.5

Titration of the hot brine with lime slurry (Figure 1) suggests the use of lime as precipitant for the heavy metal hydroxides. Saturation of the brine with respect to calcium ion precludes pH values in excess of 8.9, hence minimizing pH control requirements and producing a natural buffering action.

1/ Varies according to total ionic strength.

Accordingly, a series of tests was performed to evaluate the performance of lime treatment step in the purification of Sinclair No. 4 brine. In each test, a sample of the hot (95°C) brine was agitated for three hours with sufficient lime slurry to establish and maintain a pH value of 8.7. Samples of the liquor were separated at intervals and analyzed for major heavy metal content. The tests differed only in the extent to which atmospheric oxygen was made available for oxidation of ferrous and manganous ions:

1. Under nitrogen, to minimize oxidation.
2. In an open vessel, permitting "normal" atmospheric oxidation.
3. Under air sparge at one liter/minute to maximize air oxidation.

The results of these tests are shown on Figure 2. In all cases, precipitation of manganese, iron, zinc, and lead is immediate and complete ($\left[M^{2+}_{aq}\right] < 5$ ppm). However, lead was found to redissolve and subsequently reprecipitate during the course of the tests; the extent of redissolution and precipitation being dependent on the rate and extent of oxidation of the precipitate. Since the complete separation of lead from the brine can only be accounted for by co-precipitation/post-precipitation phenomena, and since ferrous-ferric oxidation will precede the oxidation of manganous ion, the behaviour of lead indicates that both ferrous hydroxide and hydrated manganese (III) oxide are acting as collectors for lead.

Figure 3 shows comparative settling data on the product slurries of tests (1) and (3); the reduced precipitate settles more rapidly than the oxidized precipitate.

On the basis of the above work, a 20-minute contact time, under nonoxidizing conditions, was selected for further evaluation of the lime precipitation process. The product solids were separated by filtration, washed with water, and dried at 110°C. Analytical data on the feed and product brines and the dried solid product are given in Table 3. Note that magnesium and sulfate, in addition to manganese, iron, zinc, and lead, are effectively removed from the brine. Also, as expected under the alkaline conditions of precipitation, ammonium ion is removed as free ammonia and hence is available for recovery by conventional wet scrubbing techniques.

Table 3

Purification of Brine by Precipitation of Heavy Metal Hydroxides

	Concentration		
Element	Feed Brine g/l	Product Brine g/l	Washed and Dried Product Solid Wt, %
Ba	0.223	0.207	0.002
Ca	34.6	36.6	12.4
Pb	0.139	<0.001	1.52
Li	0.255	0.261	0.06
Mg	0.150	0.0014	2.09
Mn	1.63	0.002	17.3
Fe	0.88	0.0053	11.0
Na	69	86	0.0088
Sr	0.710	0.719	0.009
K	19.1	18.7	0.007
Zn	0.497	0.004	6.03
SO_4	0.042	<0.001	-
NH_4	0.797	0.007	-

TITRATION CURVE: NORMAL (REDUCED BRINE WITH LIME SLURRY)

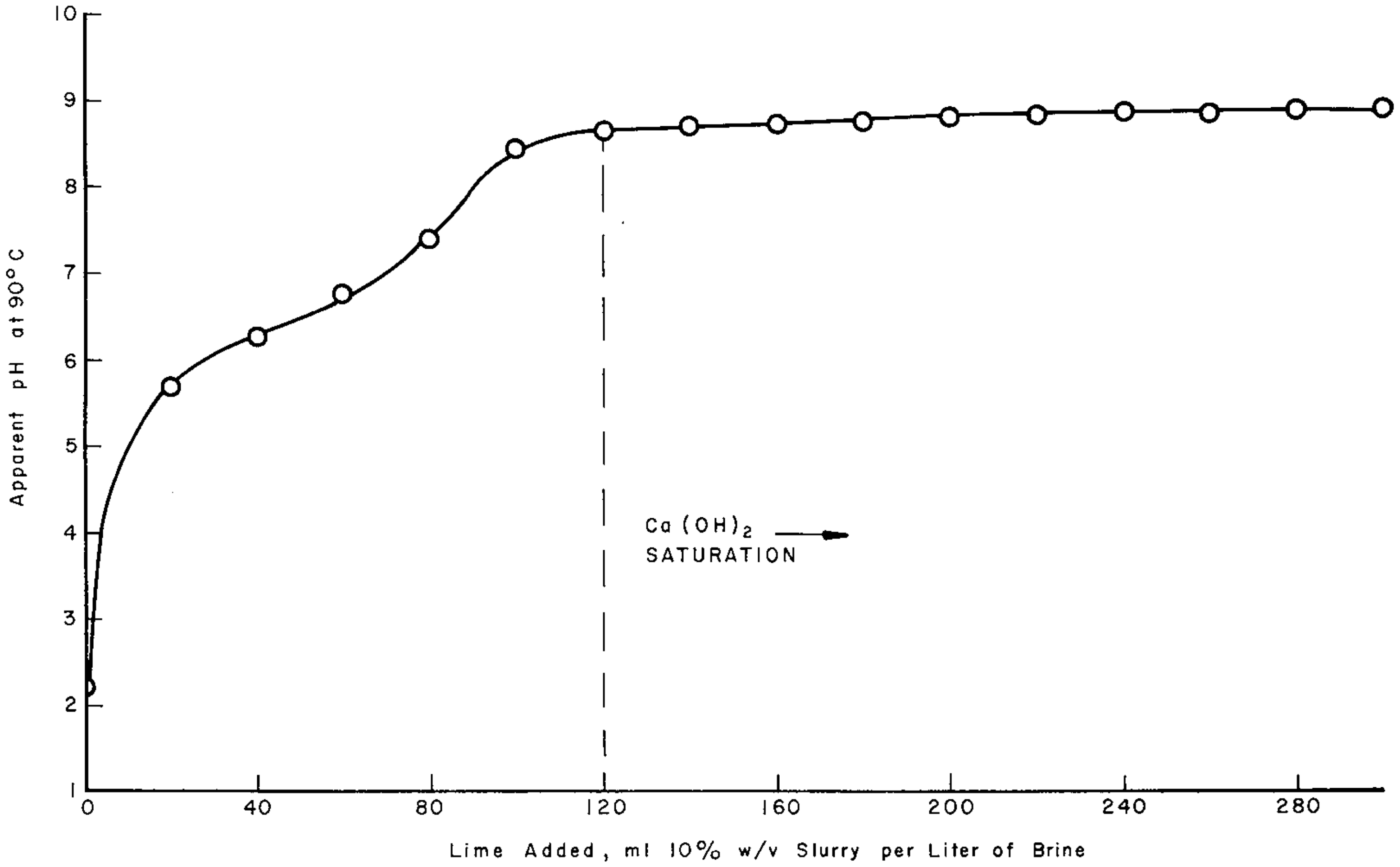


FIGURE I

hri

PRECIPITATION OF TOTAL HEAVY METALS WITH LIME, SINCLAIR # 4 BRINE

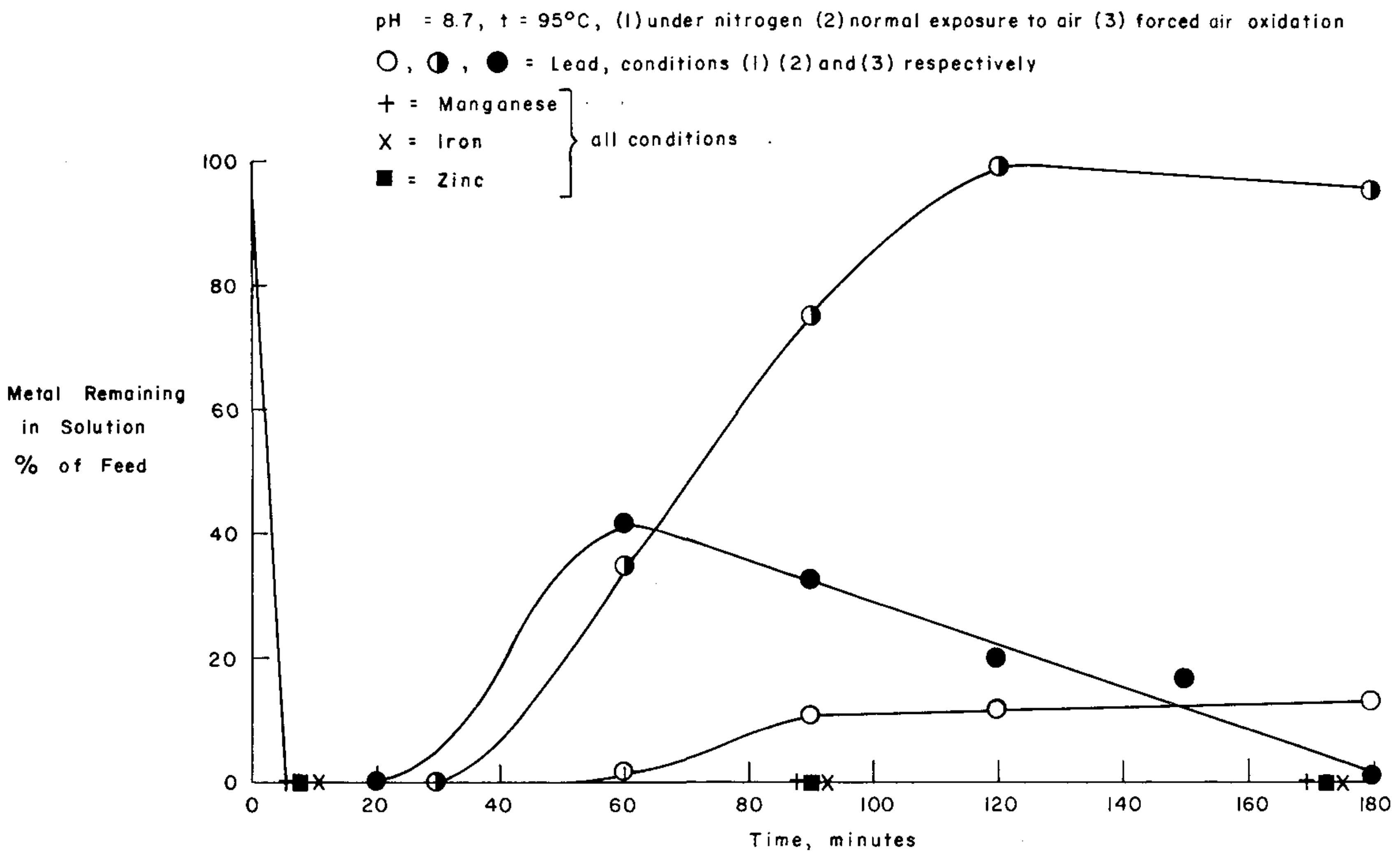


FIGURE 2

hri

SETTLING DATA FOR HEAVY METAL HYDROXIDE PRODUCTS

pH = 8.7, t = 95° C

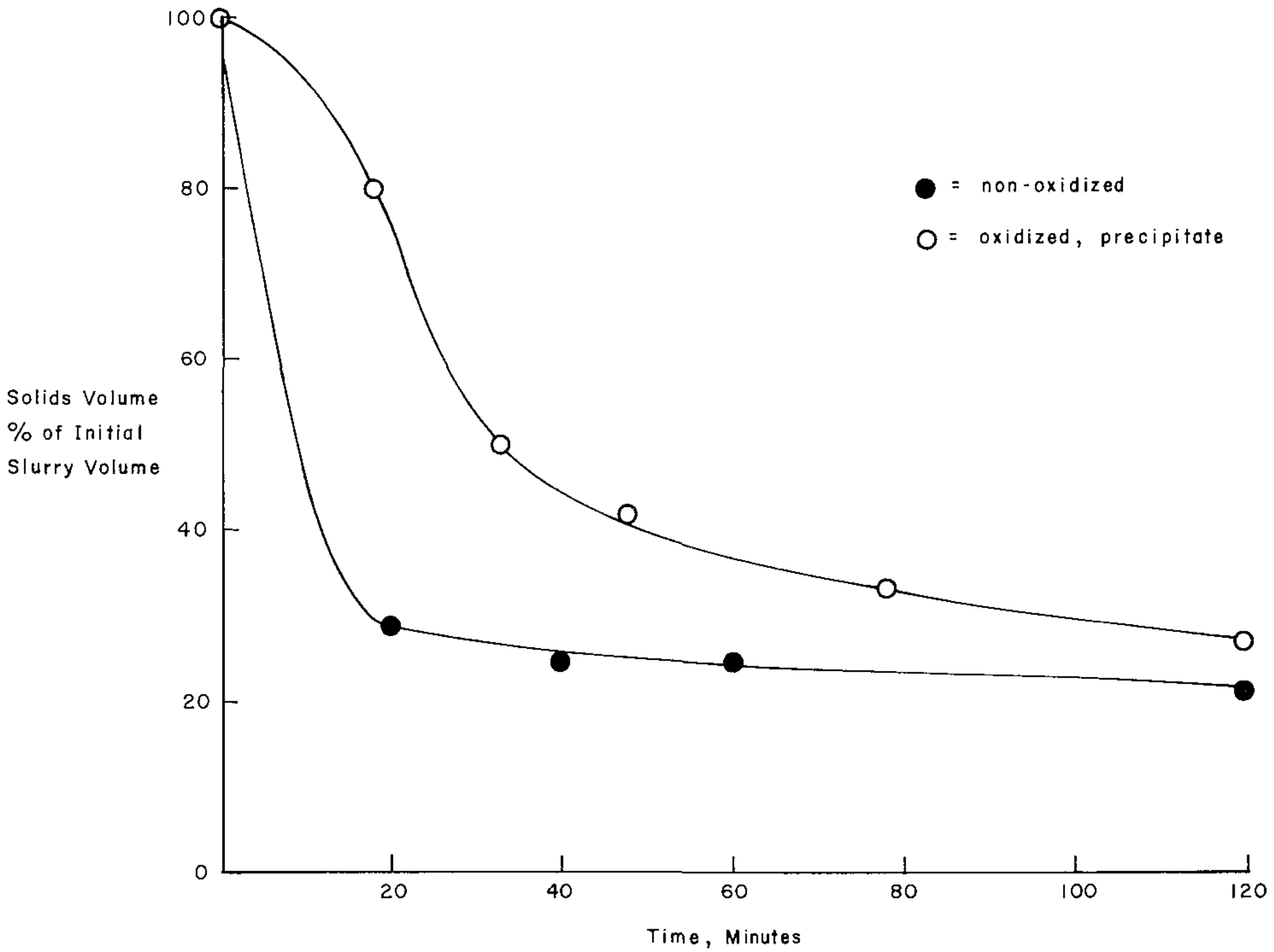


FIGURE 3

hri

SELECTIVE REMOVAL OF IRON: PRODUCTION OF MAGNETIC IRON OXIDES

The data in Table 2 suggest that iron might be selectively separated from the normal (reduced) brine by precipitation of ferrous hydroxide at pH ≈ 6, or from the oxidized brine as ferric hydroxide at lower pH values. Subsequent precipitation of manganese, lead, and zinc would thus provide a solid product much lower in iron and of greater commercial value than that produced by the process given in the preceding section.

The effect of pH on the solubilities of the major heavy metals in the normal brine was evaluated using lime (Figure 4) and ammonia (Figure 5) to control pH. No clear-cut separation is evident. In either case, a pH of 6.5 or greater is required for effective (99%) removal of iron, and even with ammonia (present to enhance zinc and manganese solubility), losses of the latter at pH = 6.5 are 14 and 22%, respectively.

Accordingly, an attempt was made to oxidize the ferrous iron to ferric iron. Four tests were performed in which brine, adjusted to pH 5.5, 6.0, 6.5, and 7.0 at 95°C, was continuously sparged with air at approximately 0.5 liters per minute for three hours.

The product solids from the tests at pH 5.5, 6.0, and 6.5 were black and highly magnetic. At pH 7, a dark brown, nonmagnetic product was obtained. Figure 6 shows the distribution of the major heavy metals at completion of the tests. At pH = 6, 97% of the iron has been removed from solution with essentially no loss of manganese, zinc, and lead.

Figure 7 compares settling data for the magnetic oxide produced at pH 6 with the ferrous hydroxide produced at pH 6.5 in the presence of ammonia. The magnetic material settles much more rapidly, and compacts to almost half the volume of the corresponding nonmagnetic material.

According to the literature (3),the production of black, magnetic hydroxides of iron by direct precipitation generally requires careful control of pH and conditions of oxidation. The technique has been applied to the separation of iron from steel mill pickle liquors and acid mine drainage liquors (4), (5), (6), but was found to occur only at pH values in excess of 7. Formation of the black product, believed to be microcrystalline hydrated magnetite, is favored by high temperatures and pressures, and in systems containing anions which form complexes with ferric ion (3). Thus, one would expect hot, high chloride systems such as Sinclair No. 4 brine to be suitable for the production of the magnetic oxide, although no indication was found in the literature of magnetic formation at pH values as low as 5.5.

Figure 8 shows the rate at which iron, initially as ferrous hydroxide, and subsequently as the black oxide, separates from 95°C brine at pH 6 under air sparge (0.5 lpm). Magnetic character was observed in the oxide within 30 minutes from the start of the test and showed no measurable increase in intensity after 60 minutes.

EFFECT OF pH ON HEAVY METAL CONTENT OF SINCLAIR # 4 BRINE

(pH adjusted with lime)

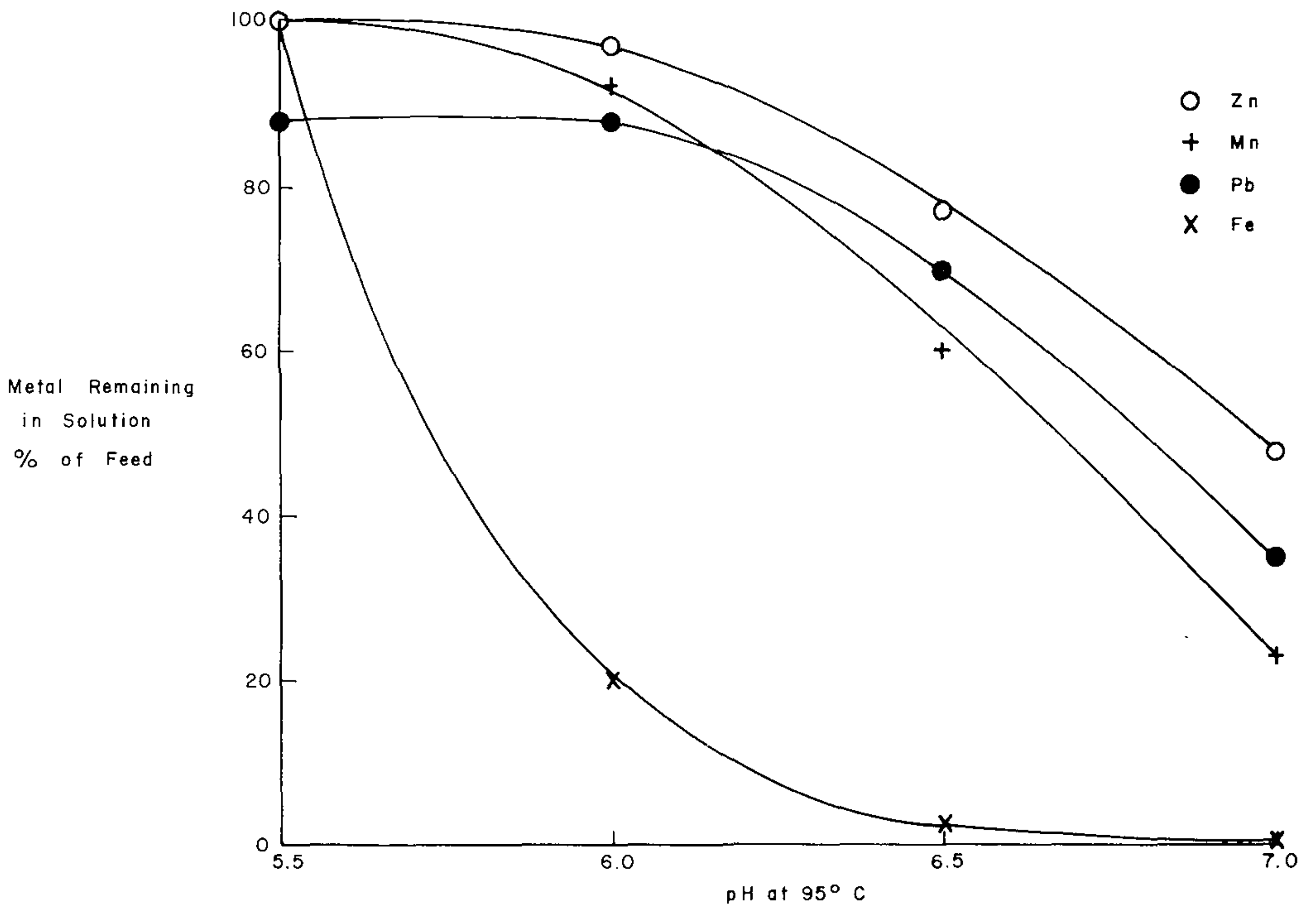


FIGURE 4
hri

EFFECT OF pH ON HEAVY METAL CONTENT OF SINCLAIR # 4 BRINE

(pH adjusted with ammonia)

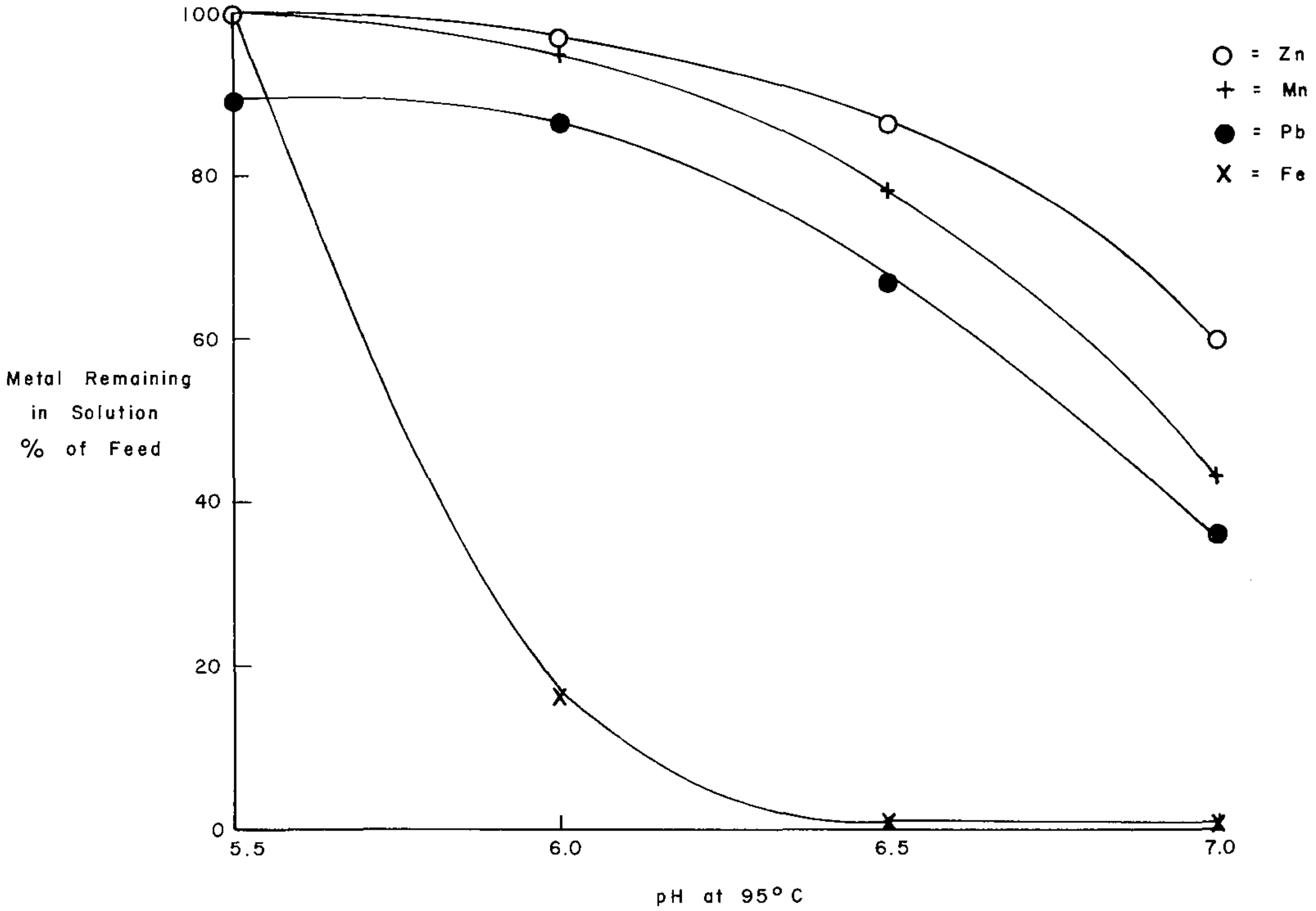


FIGURE 5

hri

MAGNETIC IRON OXIDE FORMATION: DISTRIBUTION OF HEAVY METALS

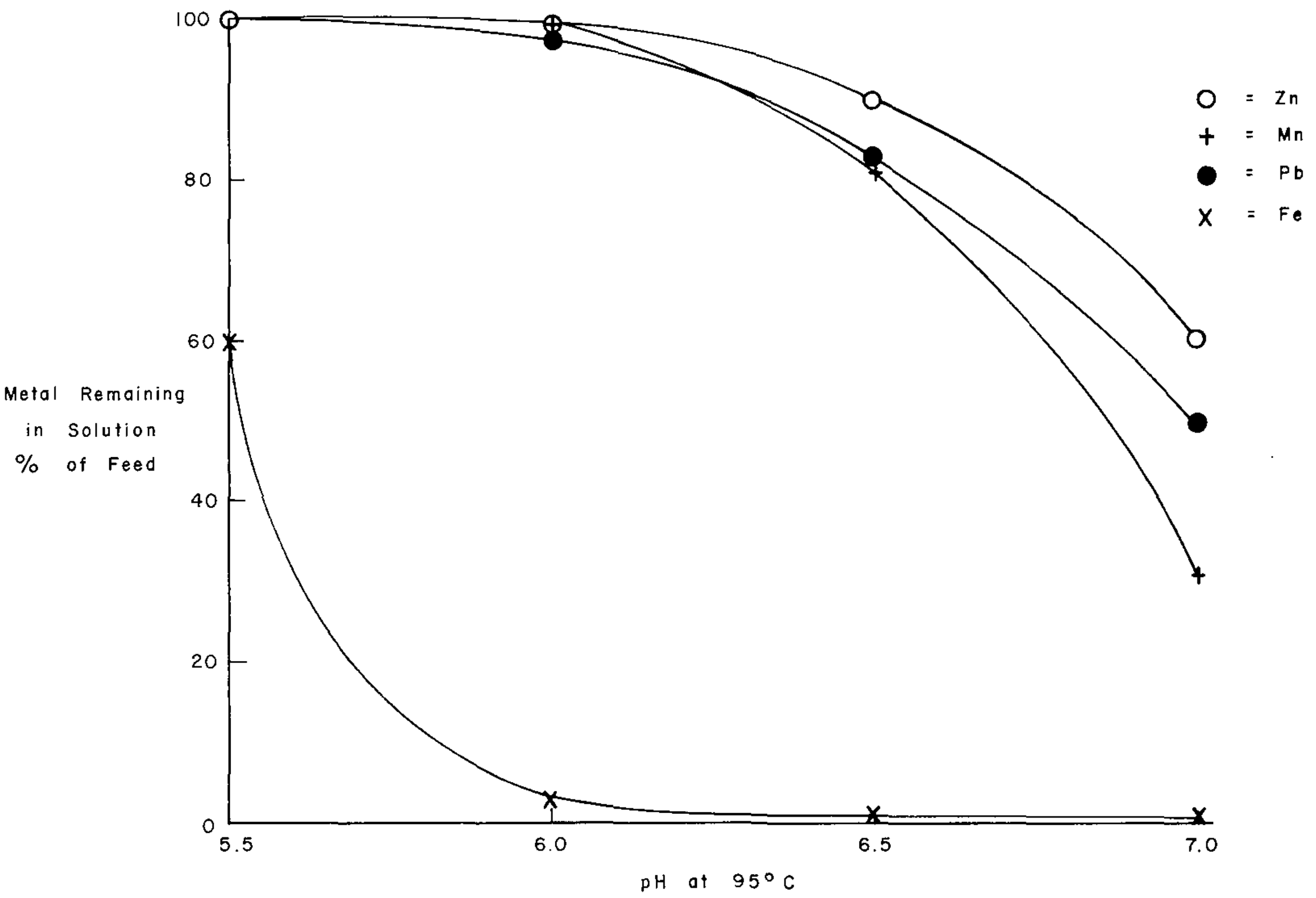


FIGURE 6
hri

SETTLING DATA FOR HYDRATED IRON OXIDE PRODUCTS

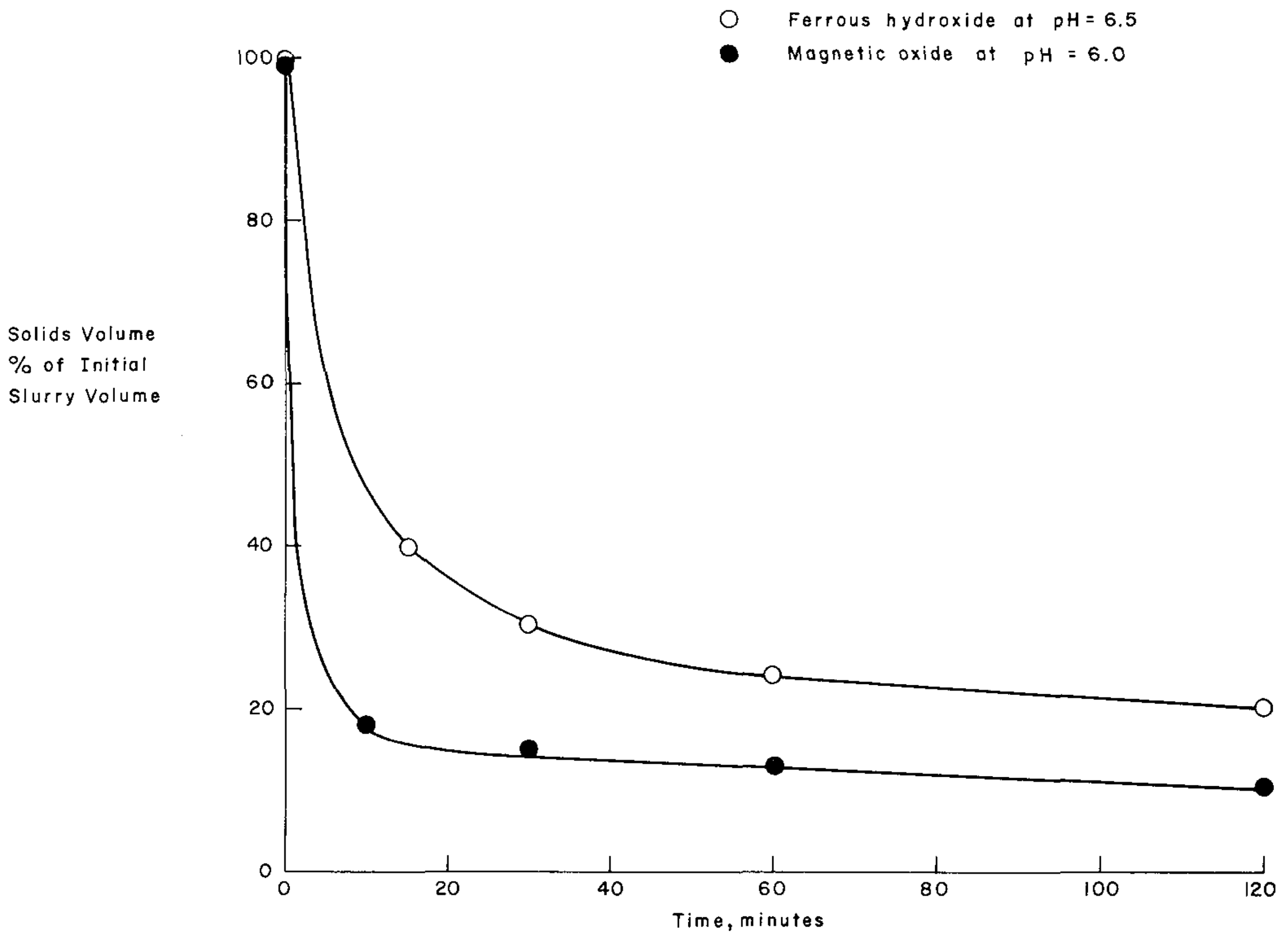


FIGURE 7

hri

RATE OF PRECIPITATION OF IRON FROM SINCLAIR #4 BRINE

pH = 6.0 t = 95° C Air at 0.5 lpm

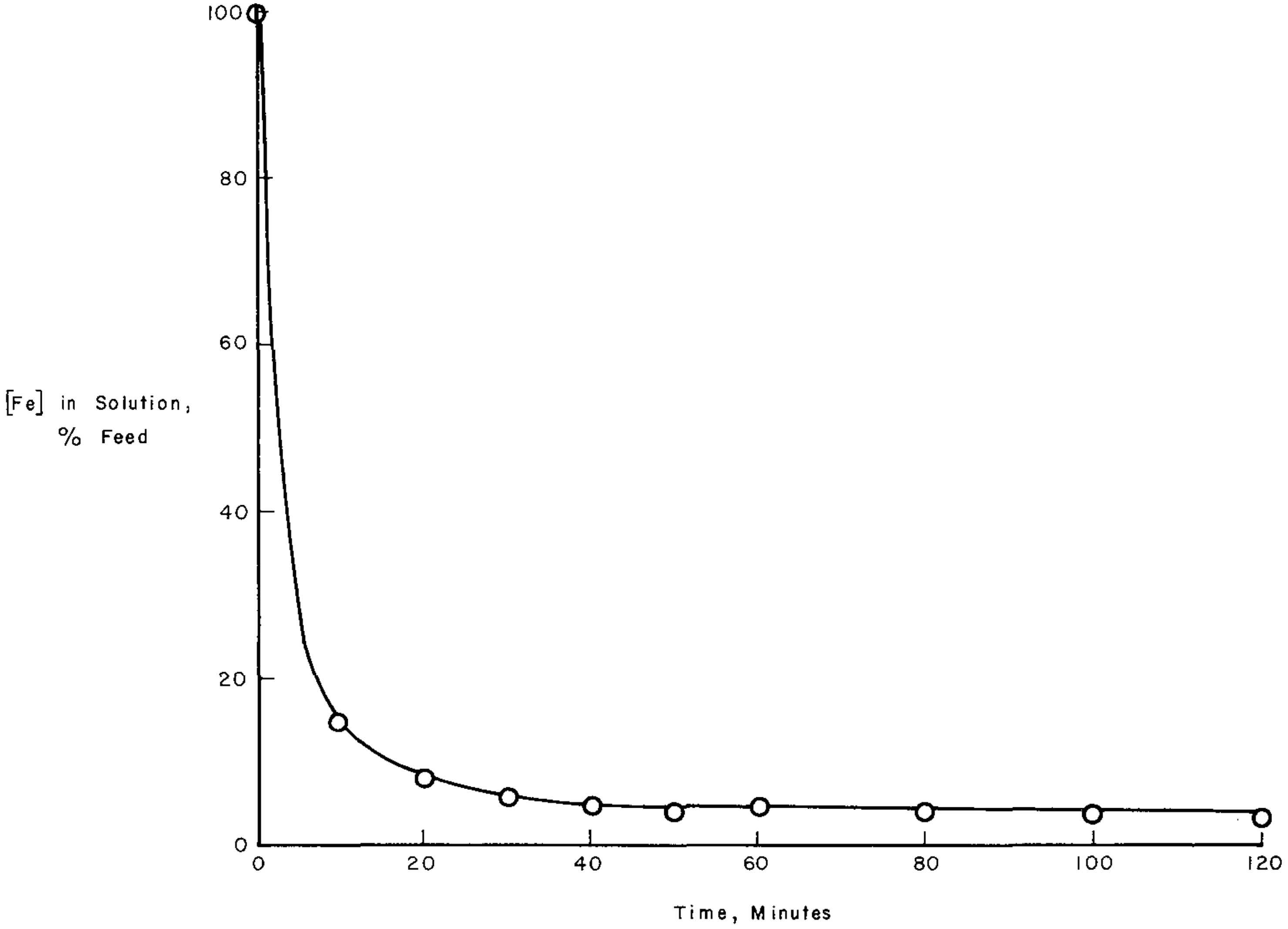


FIGURE 8
hri

REMOVAL OF MANGANESE, ZINC, AND LEAD

Iron free brine was prepared by precipitation and separation of magnetic iron oxide in accordance with the previous section. The liquor was agitated for three hours, with sufficient lime slurry added to establish and maintain a pH of 8.7. Analysis for manganese, zinc, lead, and iron was performed at intervals. Two tests were run: (1) under nitrogen to preclude oxidation of manganous ion, and (2) under a continuous air sparge of one liter per minute. Results are shown in Figures 9 and 10, respectively. As expected from the data obtained in section 3 of this report, the major difference between the tests is in the solubility of lead: more than 50% of feed under nonoxidizing conditions, but less than 5% following oxidation. Surprisingly (Figure 2), zinc shows a finite solubility (2% of feed) in the unoxidized system.

Comparative settling data for the two product solids are provided on Figure 11. Oxidation of the precipitate causes a significant reduction in settling rate, although the final volume occupied by the solids is less.

PRECIPITATION OF MANGANESE (+), ZINC (○) and LEAD (●)
FROM IRON FREE BRINE

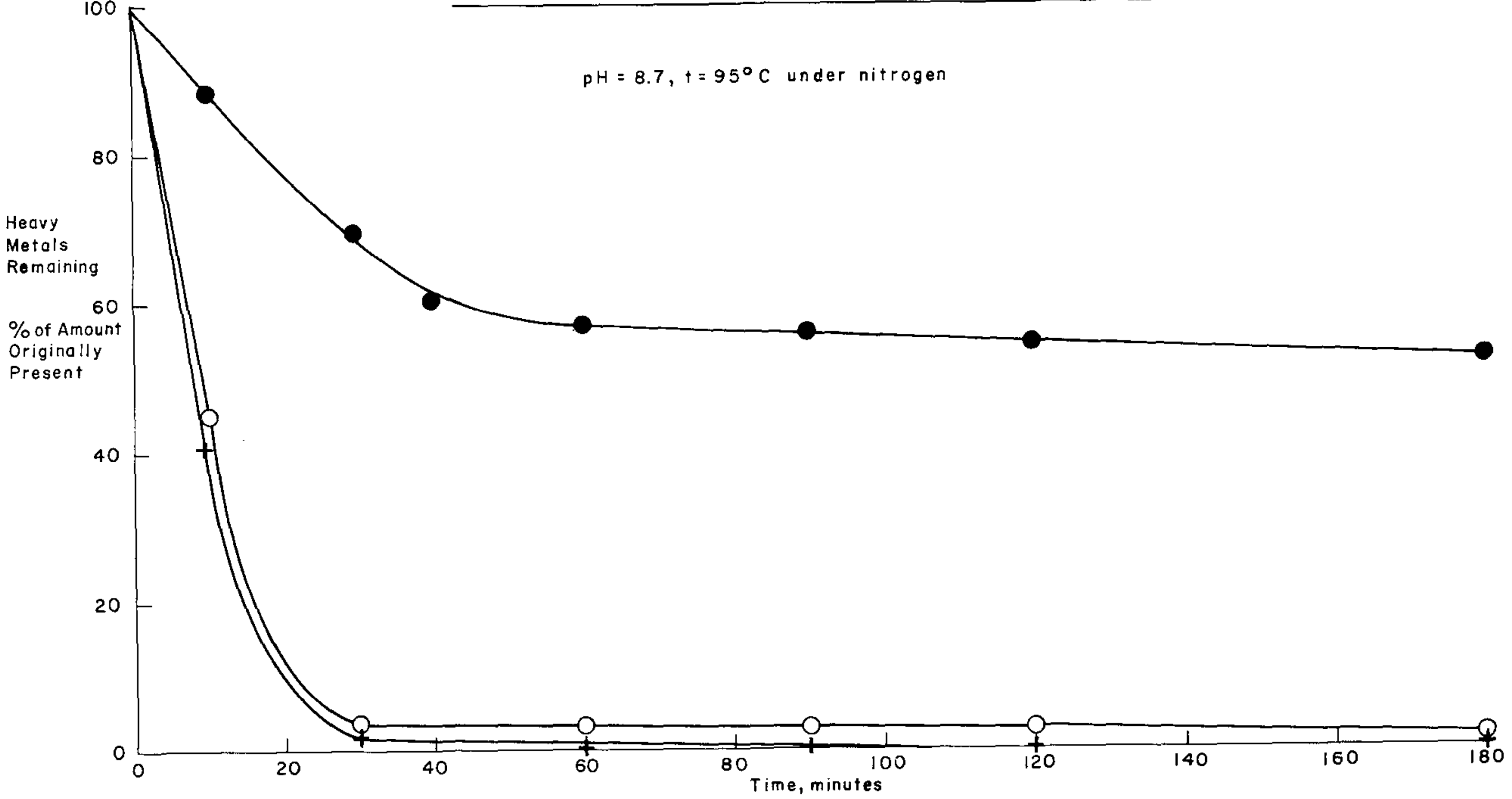


FIGURE 9

hri

PRECIPITATION OF MANGANESE (+) ZINC (○) and LEAD (●)
FROM IROM FREE BRINE

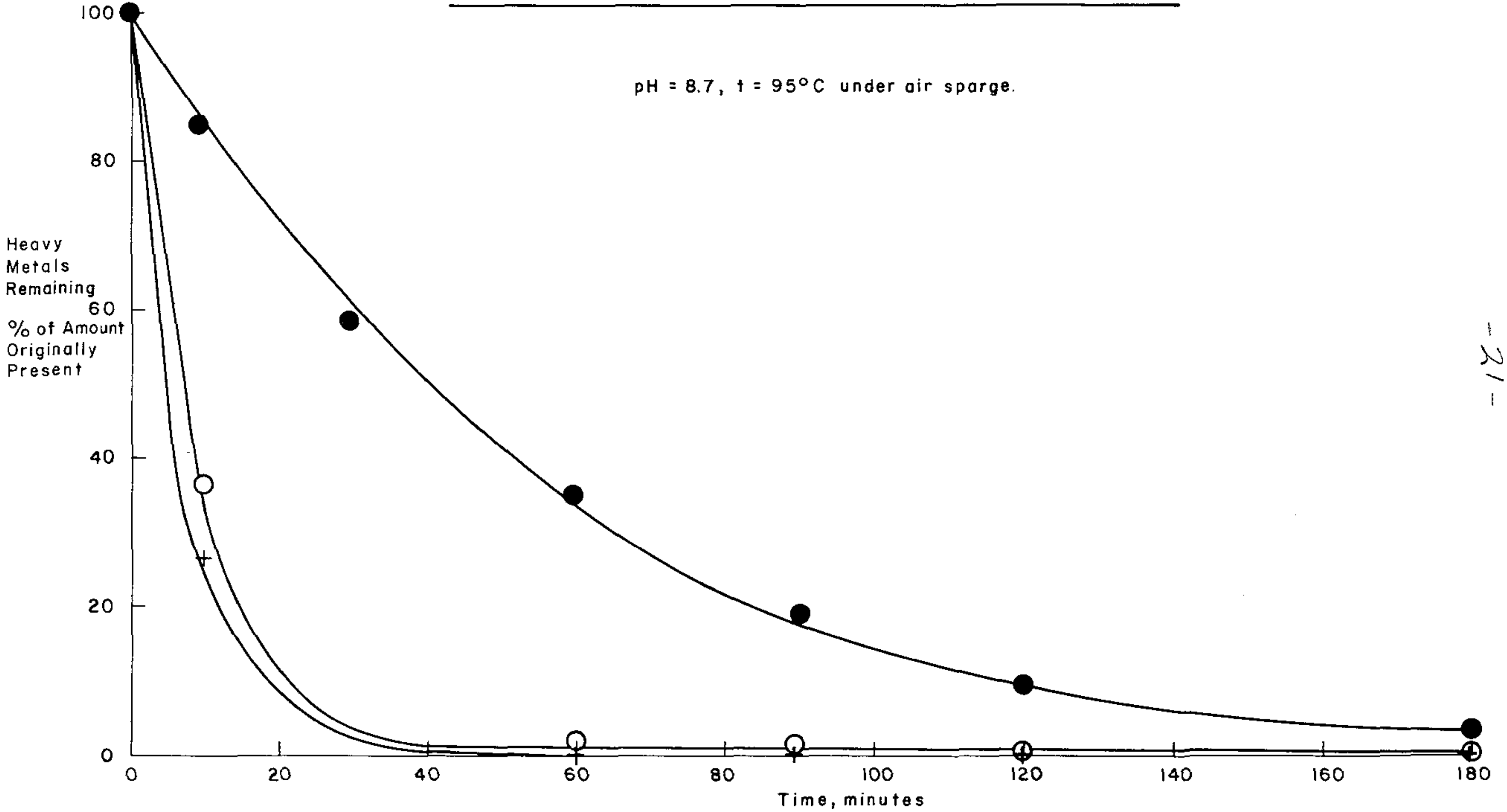


FIGURE 10

hri

SETTLING DATA FOR MANGANESE, ZINC, LEAD HYDROXIDES

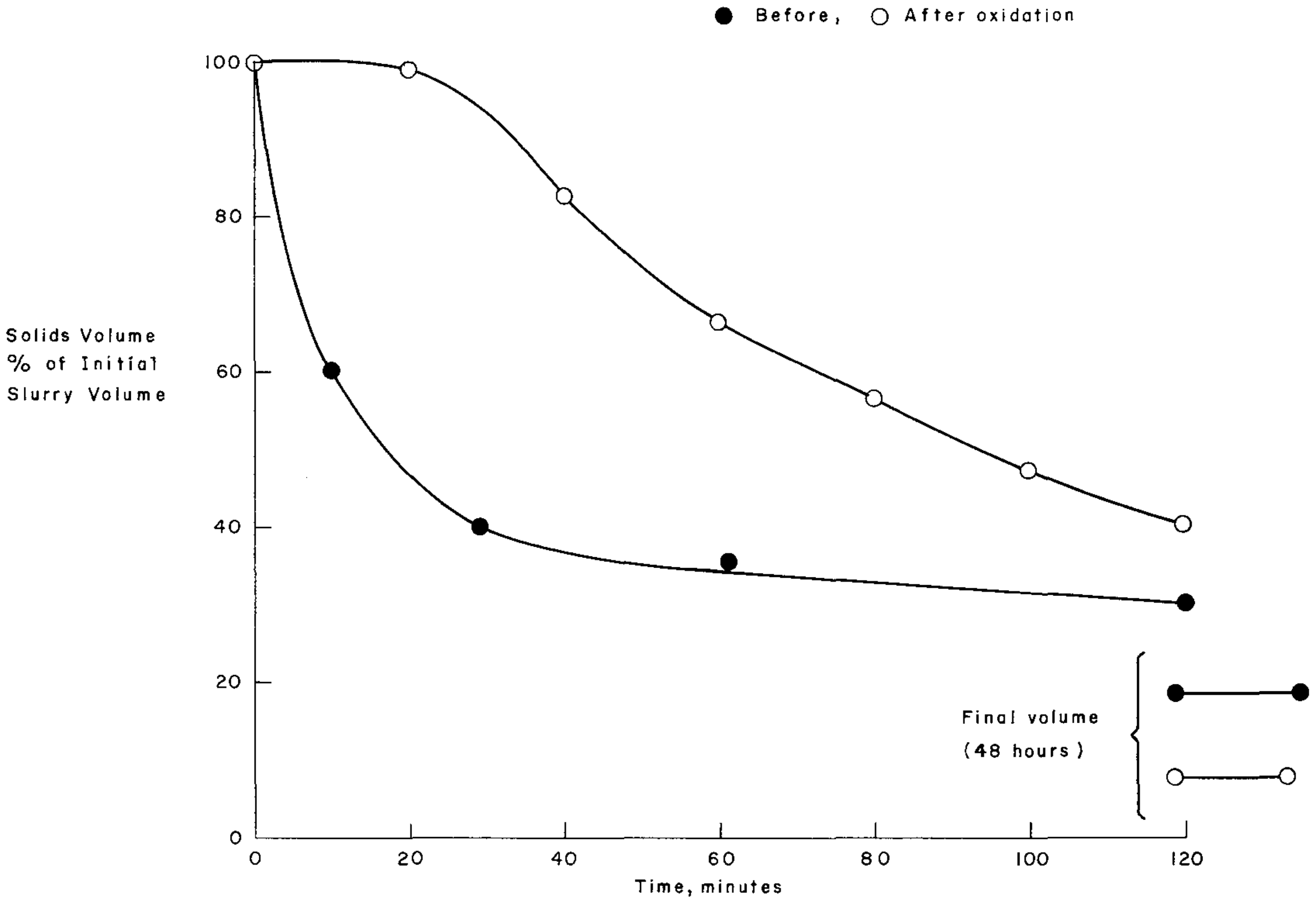


FIGURE II

hri

RECOVERY OF LITHIUM

Much has been published on the recovery of lithium values from brines. Solvent extraction into alcohol ketone mixtures has been applied effectively, although pretreatment of the brine with either ammonia (7) or urea (8) has been found necessary to prevent interference from calcium. Extraction of lithium tetrachloroferrate into di-isobutyl ketone with a water strip has been used for lithium recovery from bitterns, but requires pretreatment of the brine with hydrochloric acid and ferric chloride in order to establish extraction conditions (9).

The preferred method of recovery is based on the precipitation of lithium with aluminum hydroxide, initially proposed by Goodenough (10) and later modified by Neipert and Bon (11). In the presence of freshly precipitated aluminum hydroxide, or during the in-situ precipitation of aluminum hydroxide from the brine, lithium is reported to form an insoluble,hydrated lithium aluminate complex with an atomic ratio of 1 Li: 2-3.5 Al. Satisfactory separation of lithium requires rigorous control of the pH, typically close to neutrality, but dependent to some extent on the actual composition of the brine. Complex formation is also influenced by temperature, the preferred range being 25-50°C in the absence of magnesium (10), 50-100°C, otherwise (10, 11).

A major difficulty with the process is in the separation of the precipitate which tends to be gelatinous (average particle size, one micron) and filterable at detrimentally slow flowrates of 0.1 gal/min/ft^2 (11). Neipert and Bon have reduced the problem somewhat by precipitate recycling processes (11). Also, consumption of aluminum hydroxide is high: maximal precipitation of lithium is achieved only at Al:Li mole ratios of between 4 and 10:1.

In accordance with the above information, a series of tests was performed to establish optimal pH conditions for (1) the complete separation of lithium, and (2) the rate of settling of the precipitates from brine, using aluminum hydroxide as precipitant. In addition, tests were done to establish the optimal Al:Li ratios for lithium recovery.

The brine used in the tests was first purified by the procedure outlined in section 3 of this report and hence corresponded closely with the composition of the product brine listed in Table 3.

Figure 12 shows the effect of pH in lithium recovery. The data were obtained by simultaneous treatment of the hot ($75^{\circ}C$) agitated brine with aluminum chloride solution and lime slurry so as to maintain the desired pH to within 0.2 units during the in-situ precipitation of aluminum hydroxide. The final mole ratio of aluminum to lithium was 4:1 based on an initial lithium concentration of 250 ppm, and the slurries were agitated for one hour following aluminum addition.

Lithium precipitation is shown to be in excess of 99% of the total available in the pH range 6-8.3. Outside these limits, and particularly on the alkaline side, the efficiency of aluminum hydroxide for lithium collection falls off rapidly. It should be noted that the pH range for maximum lithium recovery is much wider than that previously reported (10, 11).

Settling data (Figure 13) for the precipitates show no clearly defined relationship to pH, but do indicate the formation of more dense precipitates under alkaline conditions.

Figure 14 shows the effect of aluminum:lithium ratios on lithium recovery. Experimental conditions were as described above, with the pH controlled at 7.5 ± 0.2. Recoveries of 99% of contained lithium were obtained at an Al:Li ratio of 3:1 (approximately 10:1 $Al_2O_3:Li_2O$ by weight). Under these conditions, the precipitate settles to 16% of the original slurry volume within one and one-half hours (Figure 15).

Table 4 provides a comparison of the lithium recoveries obtained above with those cited elsewhere in which brines of similar compositions were studied.

Table 4

Comparison of Lithium Recovery Methods

	Present Work	Goodenough (10)	Neipert and Bon (11)
pH	7.5	5.25	6.8
Temperature, °C	75	74	25
Al:Li	3.2	4.7	4.2
% Li precipitated	99.5	96	92.5

EFFECT OF pH ON PRECIPITATION OF LITHIUM WITH ALUMINUM HYDROXIDE

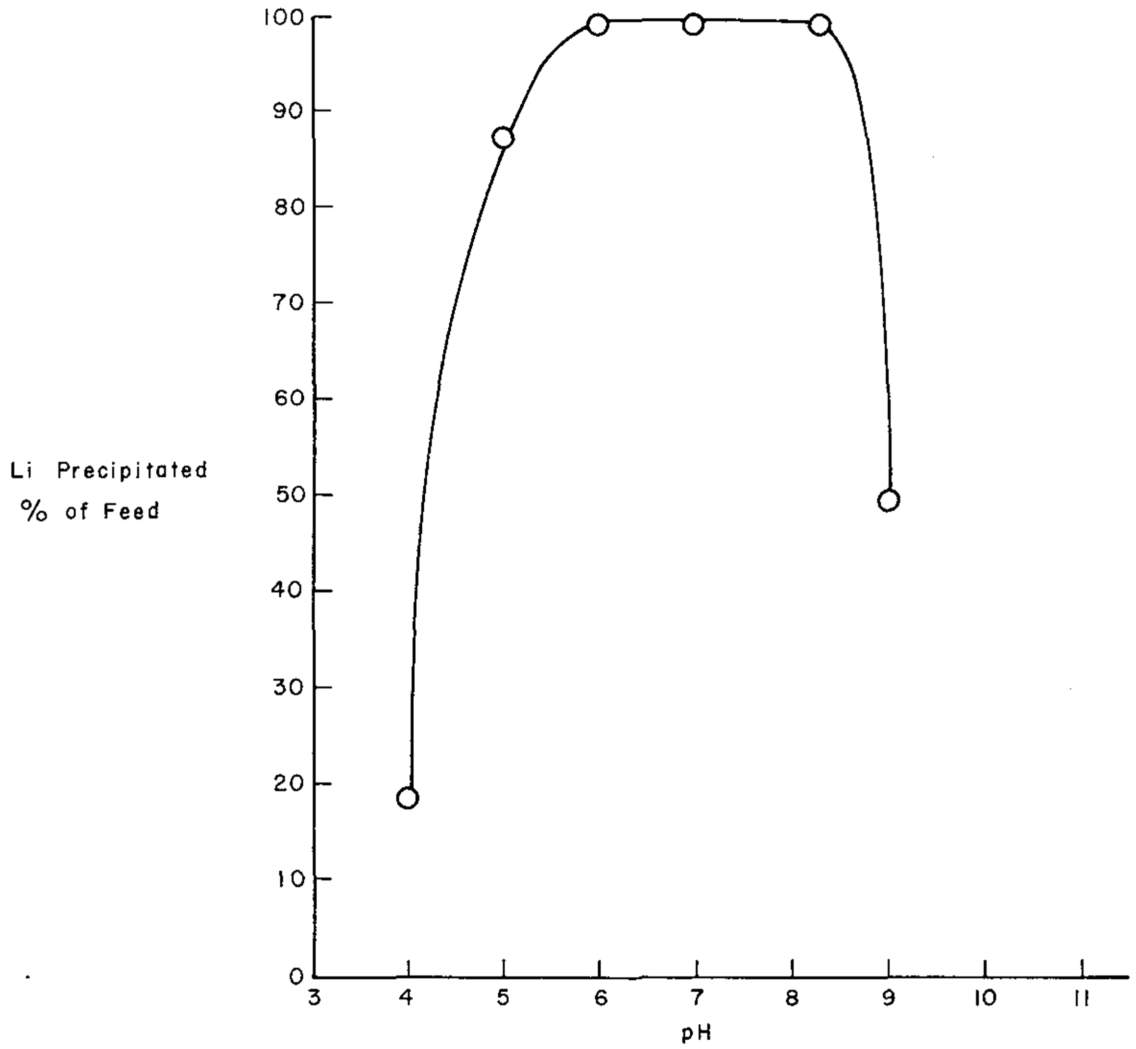


FIGURE 12

hri

SETTING DATA FOR ALUMINUM (LITHIUM) HYDROXIDES

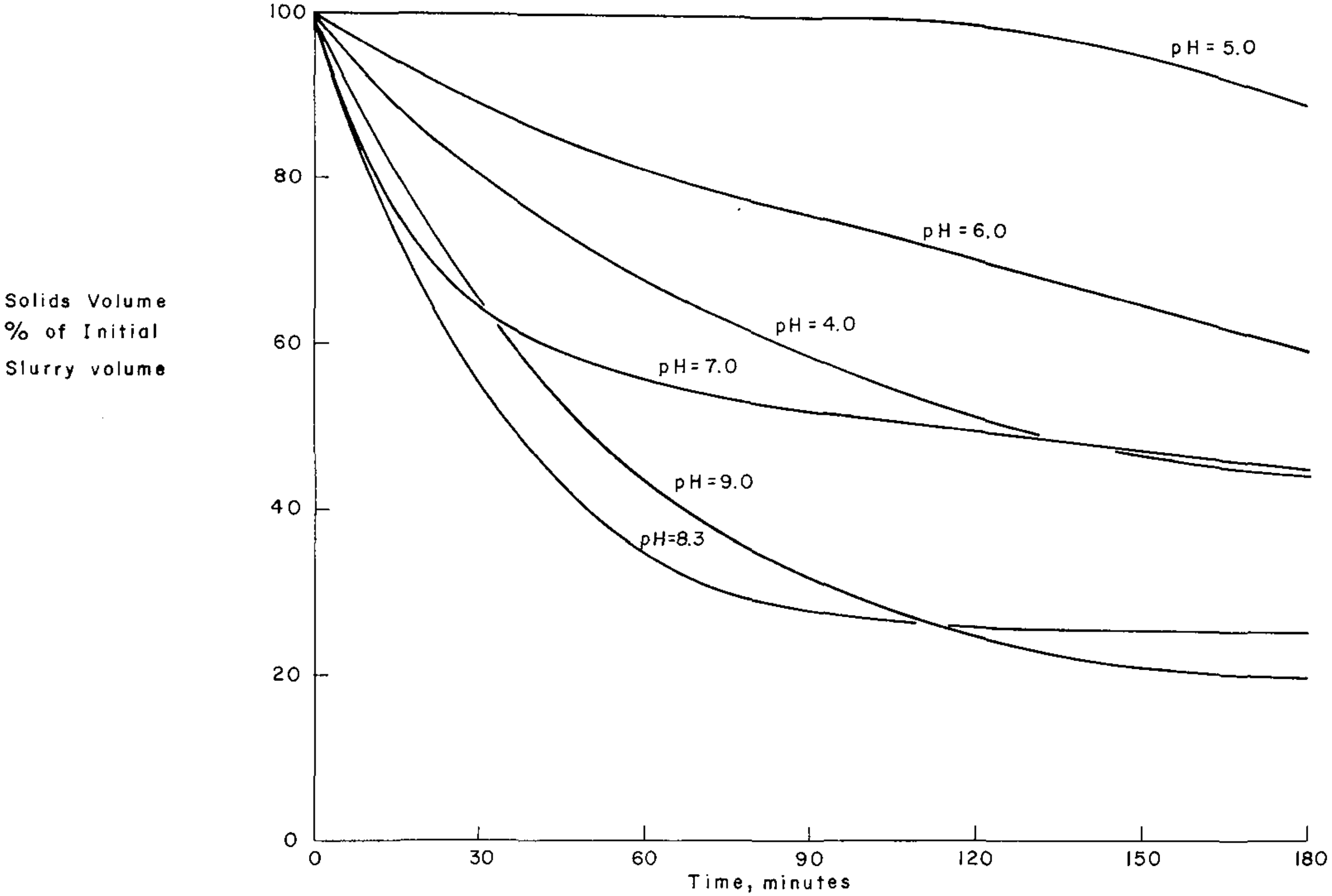


FIGURE 13

hri

EFFECT OF Al : Li RATIOS ON LITHIUM RECOVERY

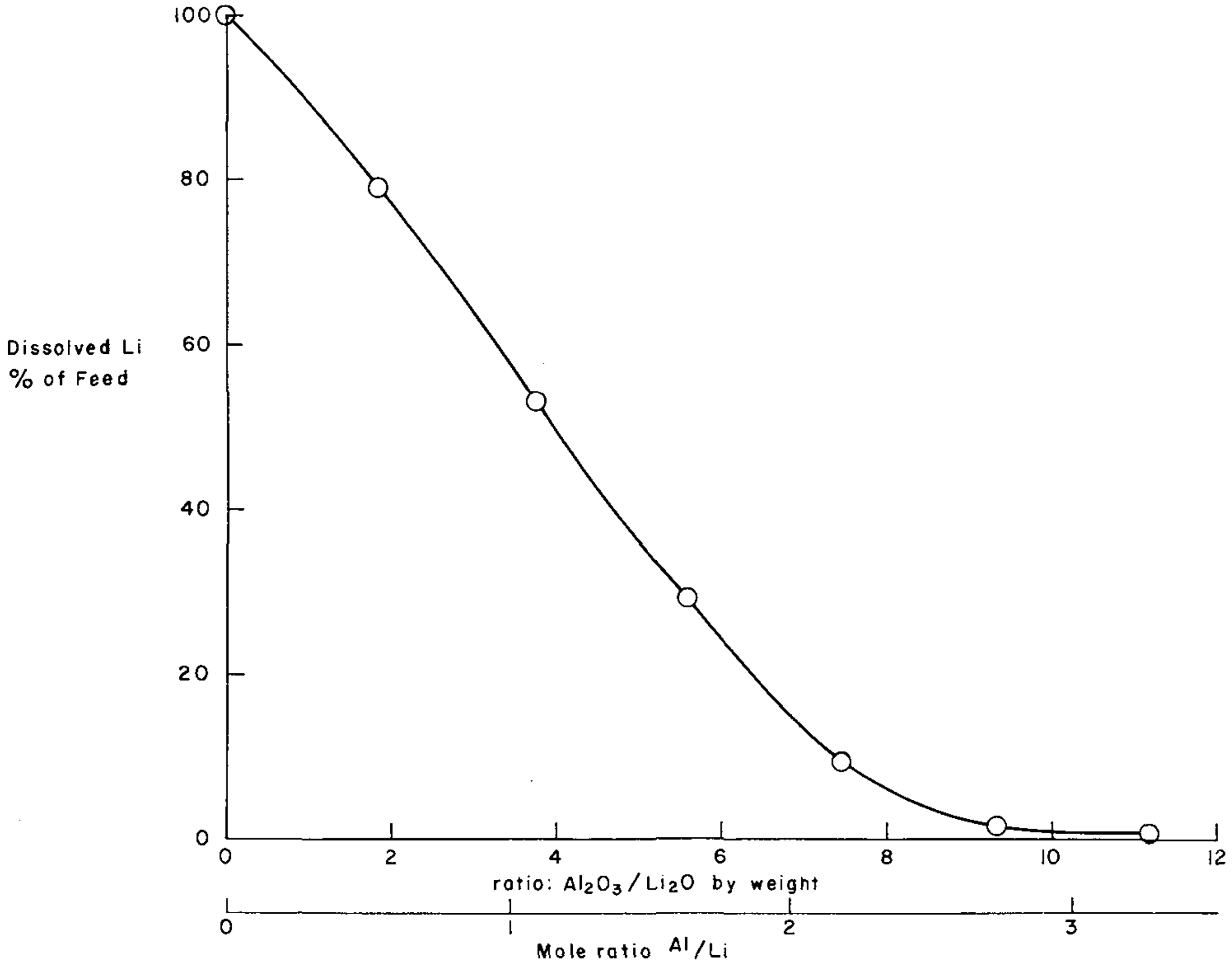


FIGURE 14

hri

SETTLING CURVE - ALUMINUM (LITHIUM) HYDROXIDE AT pH=7.5

Al : Li = 3:1

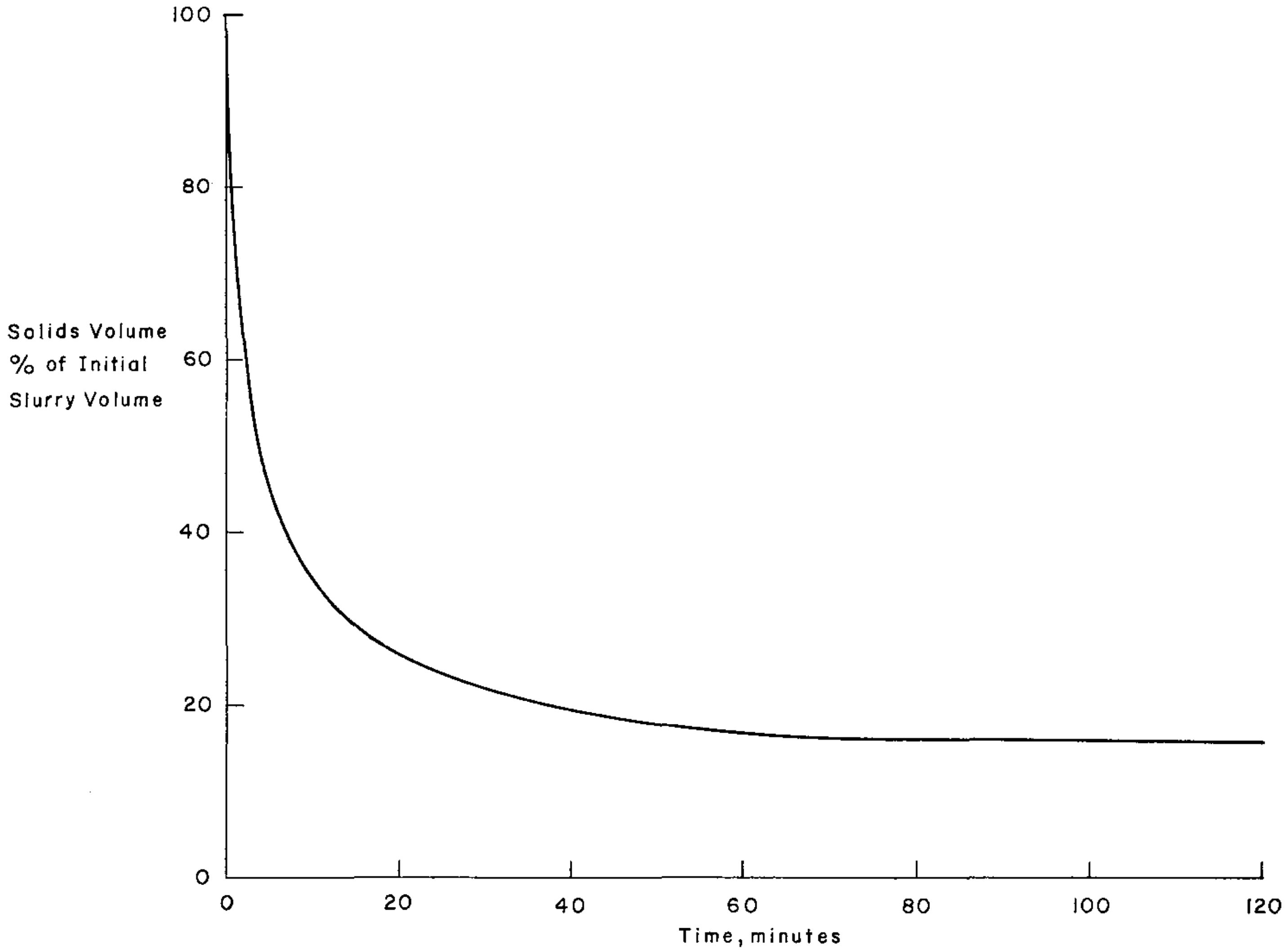


FIGURE 15

hri

RECOVERY OF STRONTIUM AND BARIUM

Table 3 shows that the brine produced by precipitation of the heavy metals with lime consists essentially of the chlorides of the alkali metals: sodium, potassium and lithium; and the alkaline earths: calcium, strontium, and barium. In the absence of massive quantities of chloride ion, separation of strontium and barium could readily be achieved by sulfate precipitation. However, the solubility of the sulfates of these metals, particularly strontium, is known to be enhanced in the presence of sodium and calcium chlorides (12, 14).

Figure 16 shows the effect on the solubility of strontium and barium produced by slurrying hot product brine (Table 3) with 10% w/v gypsum. Precipitation of barium is slow and incomplete. The system appears to stabilize after 40 minutes of contact at which time just over 60% of the barium, but only 2% of the strontium values, have been precipitated (13).

Using sodium sulfate (Figure 17), precipitation of barium and strontium is determined, as expected, by the total dissolved sulfate present. At a mole ratio of added sulfate to total barium of just under 3:1, greater than 75% of the barium can be removed as pure (i.e., strontium free), barium sulfate.

PRECIPITATION OF BARIUM AND STRONTIUM WITH GYPSUM

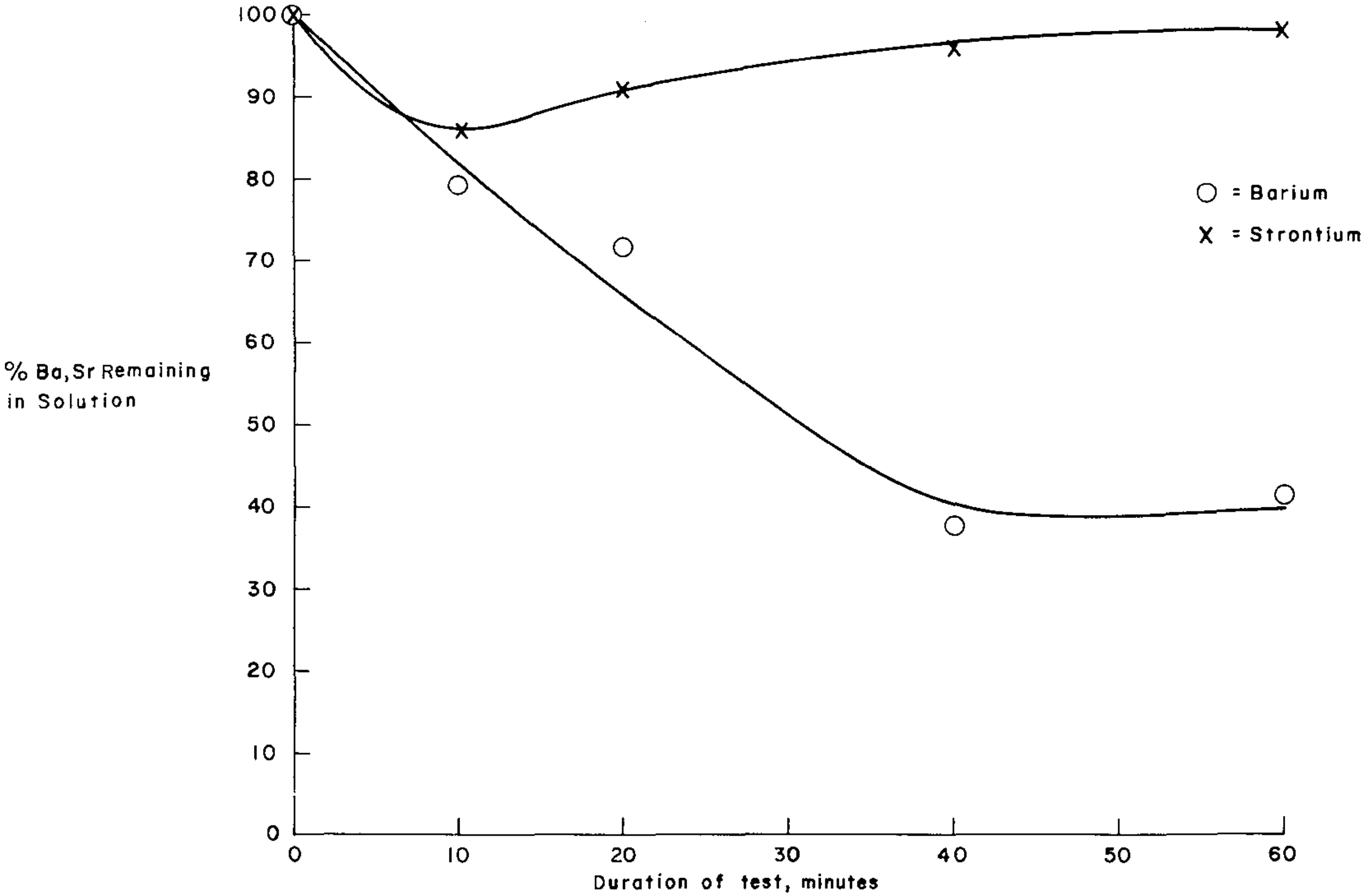


FIGURE 16

hri

PRECIPITATION OF BARIUM AND STRONTIUM WITH SODIUM SULFATE

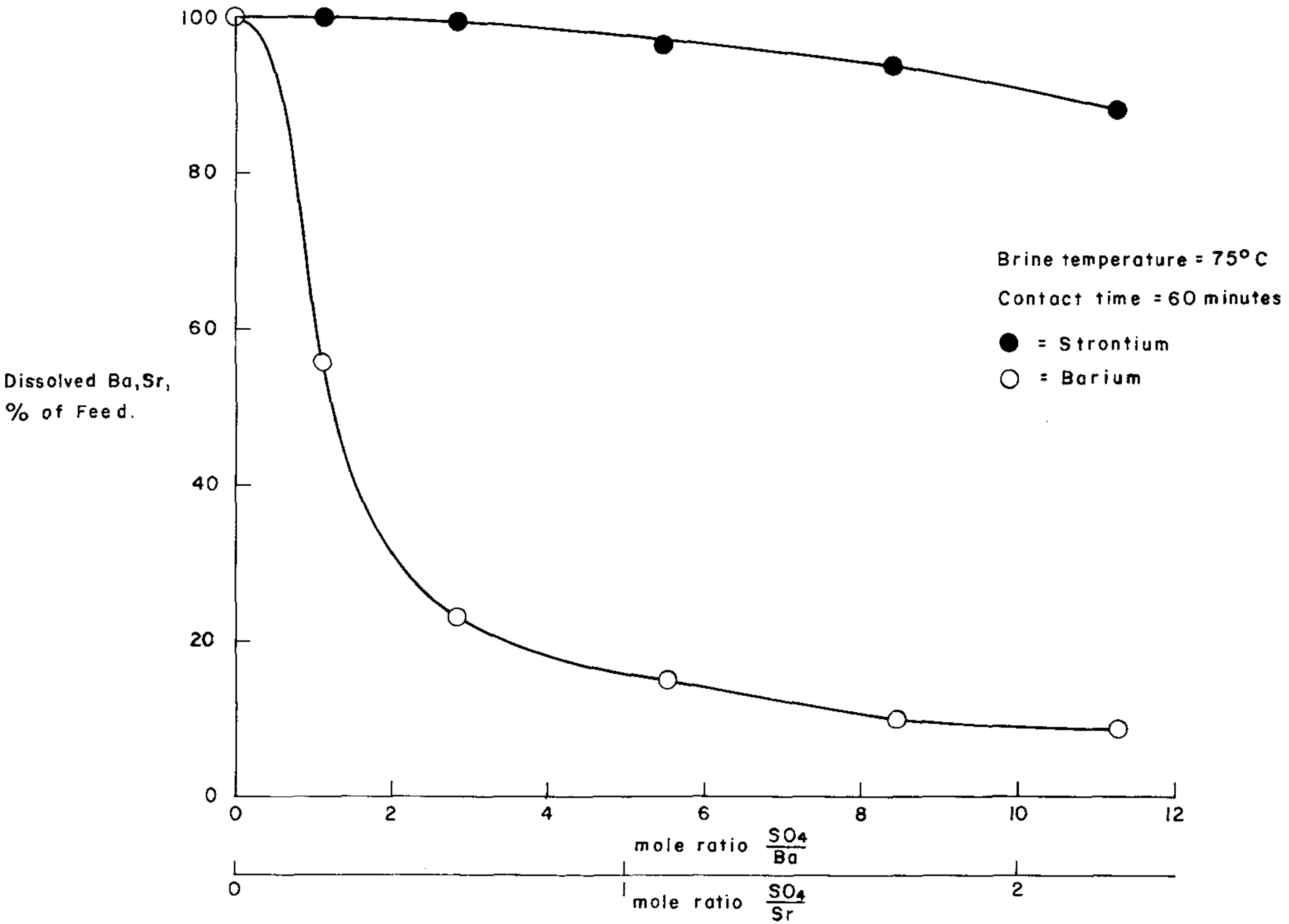


FIGURE 17

hri

EVAPORATION STUDIES: PRODUCTION OF PURE SODIUM AND POTASSIUM CHLORIDES

A brief evaluation of salt recoveries, using simulated solar pond conditions, was undertaken to illustrate the effectiveness of pre-purification of the brine as the quality of the product salt.

Crude (feed) and purified brines corresponding to the compositions given in Table 3 were used. The brines were exposed in open vessels to artifically generated wind speeds of 5-10 mph and were maintained at temperatures of 85-90^{o}F by radiant heaters.

Figure 18 shows the rate of change of various parameters during evaporations of the purified brine. The stepped nature of the curves results from intermittent manual breaking of surface crusts formed during the evaporation process. Table 5 compares the purity of the product salts. Total impurities in the product salt are reduced from 0.27 to 0.01% by pre-purification of the brine. Not only is contamination by the major heavy metals (manganese, iron, zinc, and lead) substantially reduced, but also that of the trace elements (in particular, aluminum, boron, arsenic, selenium, chromium, molybdenum, and tungsten).

Figure 19 shows a flowsheet for the separation and recovery of potassium and sodium chloride values from the brine by selective crystallization. The data were compiled from equilibrium diagrams for the quaternary system $NaCl-KCl-CaCl_2-H_2O$ at 18^{o}C and 95^{o}C (12),and are normalized to an initial brine feed weight of 10,000 units. Recovery of high grade potassium chloride depends upon the availability of hot (95^{o}C) brine for leaching potassium values from the sylvinite produced during the final evaporation, which makes the system uniquely applicable to the hot, concentrated brines, such as Sinclair No. 4.

Table 5

Analysis of Salt Products From Normal and Purified Sinclair No. 4 Brine
(Mass Spectral Data)

Element	Normal Product Salt	Purified Product Salt	Element	Normal Product Salt	Purified Product Salt	Element	Normal Product Salt	Purified Product Salt	Element	Normal Product Salt	Purified Product Salt
Ag	0.07	0.07	Cr	8.8	0.57	Mo	150	4.0	Ta	0.28	0.30
Al	210	0.34	Cs	33	0.44	Na	Maj.	Maj.	Te	<0.13	<0.10
As	35	2.9	Cu	14	0.37	Nb	0.69	0.16	Th	<0.80	<0.80
B	160	22				Ni	3.5	0.04	Ti	62	0.14
Ba	98	26	Fe	530	7.7	P	25	0.12	Tl	0.11	0.42
Be	0.17	<0.30	Ga	7.7	< 0.10	Pb	4.0	0.035	U	<0.58	<0.58
Bi	<0.88	<0.88	Ge	<0.10	<0.10	Rb	25	40	V	28	<0.10
Br	7.9	45	I	12	1.6				W	110	2.9
Ca	Maj.	Maj.	K	Maj.	Maj.	Sb	7.7	<0.10	Y	0.96	0.12
Cd	<0.17	0.18	La	0.15	-	Se	0.89	0.38	Zn	24	< 0.10
Ce	6.5	0.23	Li	940	40	Si	4.9	5.3	Zr	2.0	0.05
Cl	Maj.	Maj.	Mg	≈0.13%	<9.0	Sn	0.41	0.19			
Co	<0.58	<0.10	Mn	20	0.02	Sr	93	86			
									Total	2740	107.9

Elements reported as parts-per-million by weight, unless otherwise stated.
Maj. = Major quantities present.
Total = Sum of all contaminants except Li, Rb, Cs, Ca, Sr, and Ba.

SIMULATED SOLAR EVAPORATION, PURIFIED BRINE

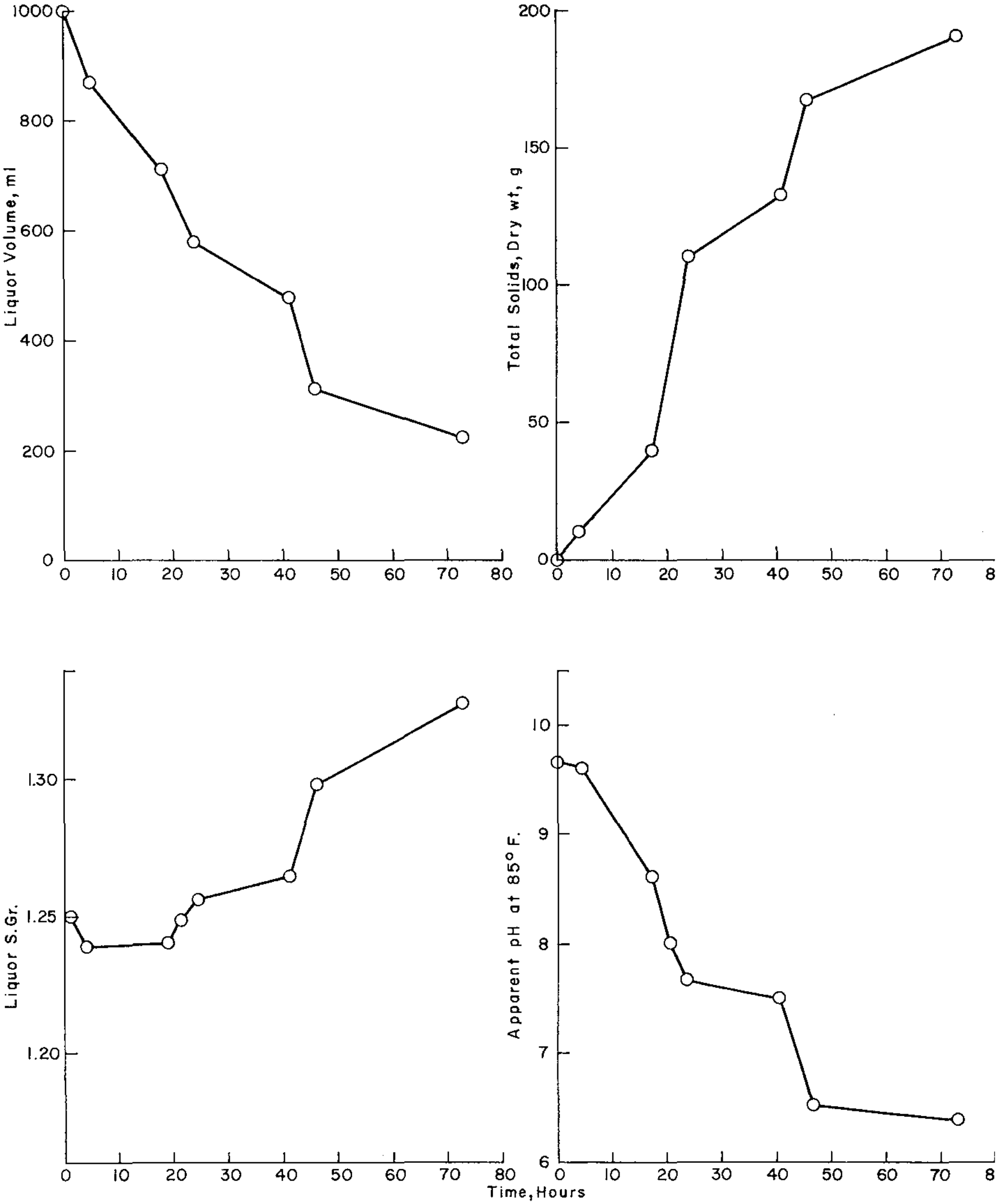
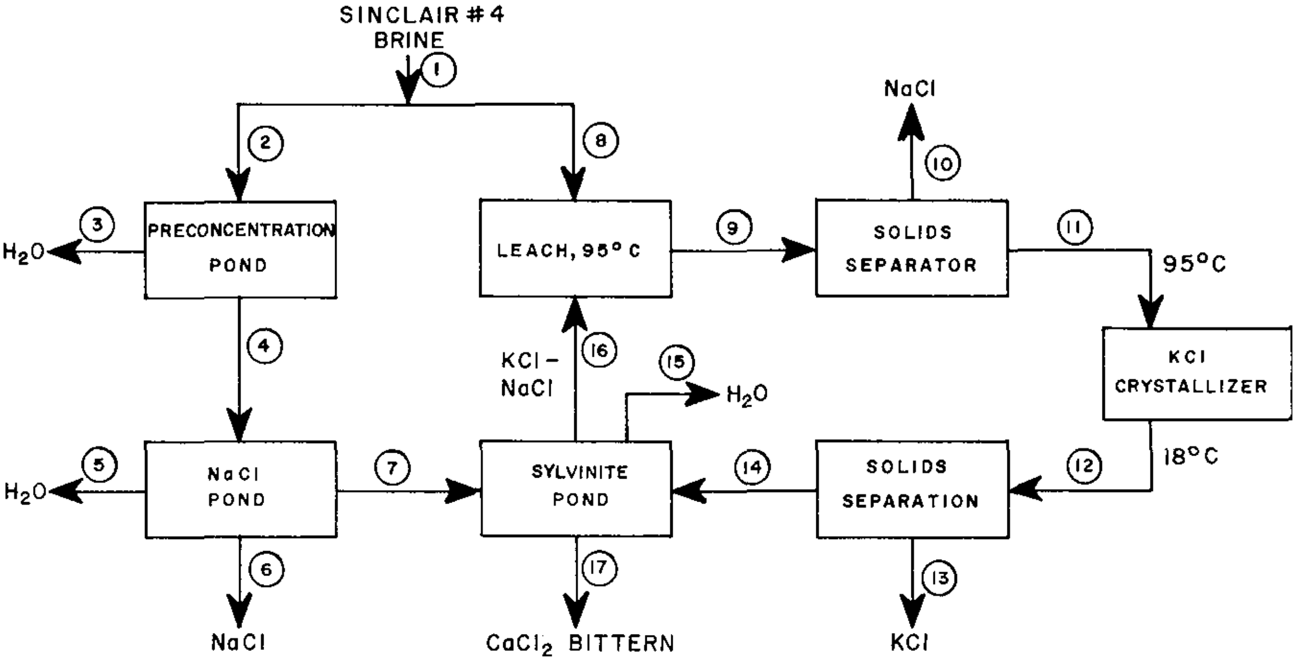


FIGURE 18

hri

FLOWSHEET FOR KCl RECOVERY



STREAM		①		②		③		④		⑤		⑥		⑦		⑧		⑨	
		Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%
H_2O VAPOR						1588				2653									
BRINE	H_2O	7798	77.98	6373				4785	72.67					2132	67.09	1425		1425	62.47
	NaCl	1235	12.35	1009				1009	15.32					255	8.02	226		319	13.99
	KCl	258	2.58	211				211	3.20					211	6.64	47		408	17.89
	$CaCl_2$	709	7.09	580				580	8.81					580	18.25	129		129	5.65
SOLIDS	NaCl												754					473	
	KCl																		

STREAM		⑩		⑪		⑫		⑬		⑭		⑮		⑯		⑰	
		Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%	Wt.	%
H_2O VAPOR												2582					
BRINE	H_2O			1425		1425	68.87			14.25	68.87					975	56.10
	NaCl			319		319	15.42			319	15.42					8	0.46
	KCl			408		196	9.47			196	9.47					46	2.65
	$CaCl_2$			129		129	6.23			129	6.23					709	40.79
SOLIDS	NaCl	473												566			
	KCl					212		212						361	38.9		

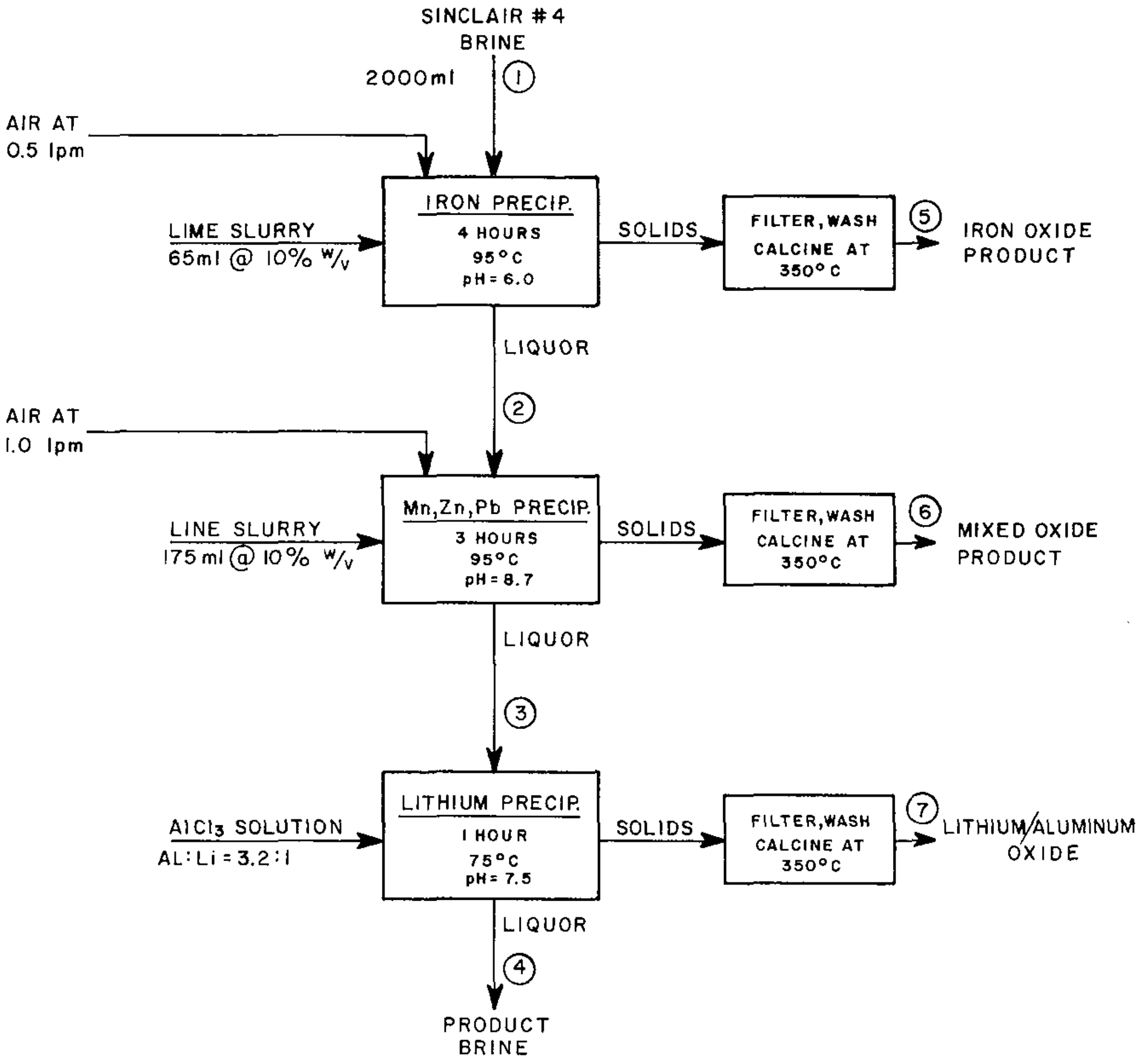
FIGURE 19

hri

FLOWSHEET FOR BRINE PURIFICATION

The flowsheet shown in Figure 20 represents a batch evaluation of the processes developed in the various sections of this report for the selective separation of iron, the remaining major heavy metals, and lithium from Sinclair No. 4 brine. Note that the final product brine has undergone further purification during lithium precipitation by virtue of the ability of aluminum hydroxide to coprecipitate the heavy metal hydroxides.

FLOWSHEET FOR BRINE PURIFICATION



LIQUOR	CONCENTRATION, PPM				
	Mn	Fe	Zn	Pb	Li
① FEED	2000	1810	805	120	
② IRON PRECIP. DISCH.	2000	20	780	110	
③ Mn PRECIP. DISCH.	<1.0	1.0	5.0	5.0	440
④ PRODUCT BRINE	<1.0	<1.0	<1.0	<1.0	4.6

SOLID	Wt., g.	CONCENTRATION, %				
		Mn	Fe	Zn	Pb	Li
⑤ IRON OXIDE Product	4.9	<0.1	68.0	0.9	0.4	–
⑥ MIXED OXIDE Product	8.5	47.3	0.6	18.2	2.8	–
⑦ LITHIUM/ALUMINUM Oxide	–	–	–	–	–	3.7

FIGURE 20

hri

Bibliography

1. Meites, L., Handbook of Analytical Chemistry, 1st Edition, McGraw-Hill, 1963.
2. Weist, R. C., Handbook of Chemistry and Physics, 51st Edition, The Chemical Rubber Co., 1970.
3. Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmaus-Green & Co., 1964.
4. Rathmell, R. K., U. S. Patent 3,261,665, to E. I. duPont.
5. Svanks, K. and Shumate, K. S., Factors Controlling Sludge Density During Acid Mine Drainage Neutralization, State of Ohio Water Resources Center, Ohio State University, 1973.
6. Bituminous Coal Research, Inc., Studies on the Densification of Coal Mine Drainage Sludge, for Environmental Protection Agency, Project 14010 EJT, Sept. 1971.
7. Goodenaugh, R. D. and Gaska, R. A., U. S. 3,307,922, to Dow Chemical Co., 1967.
8. Ibid, U. S. 3,306,712, 1967.
9. Nalli, J. R. and Arthur, T. E. Jr., U. S. 3,537,813, to Lithium Corp. of America, 1970.
10. Goodenaugh, R. D., U. S. 2,964,381, to Dow Chemical Co., 1960.
11. Neipert, M. P. and Bon, C. D., U. S. 3,306,700, to Dow Chemical Co., 1967.
12. Seidell, A., Solubilities of Inorganic and Metal-Organic Compounds, Volume II, American Chemical Society, 1958.
13. Goodenaugh, R. D., U. S. 3,029,133, to Dow Chemical Co., 1962.
14. Davis, J. W., and Collins, A. G., Environ. Science Technology, Vol. 5, ppgs. 1039-1043, 1971.