



Potash Recovery From Process and Waste Brines by Solar Evaporation and Flotation

By D. G. Foot, Jr., J. L. Huiatt, and L. J. Froisland

With an Economic Evaluation by Deborah A. Kramer



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	kg	kilogram
d/wk	day per week	lb	pound
d/yr	day per year	lb/d	pound per day
°F	degree Fahrenheit	lb/h	pound per hour
ft	foot	lb/ton	pound per short ton
ft/s	foot per second	min	minute
g	gram	mol pct	mol percent
gal	gallon	mph	mile per hour
g/cm ³	gram per cubic centimeter	pct	percent
h	hour	ton/d	short ton per day
h/d	hour per day	wt pct	weight percent
in	inch	yr	year
in/yr	inch per year		

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By D. G. Foot, Jr.,¹ J. L. Huiatt,² and L. J. Froisland³

With an Economic Evaluation by Deborah A. Kramer

ABSTRACT

The Bureau of Mines investigated energy-efficient methods for recovering potash values from process and waste brines. Laboratory pan evaporation of four chloride brines produced crude salts containing predominantly sylvite, halite, and carnallite. Six sulfate-chloride brines produced crude salts containing primarily schoenite, kainite, leonite, sylvite, carnallite, and halite. Potash grades ranged from 7.2 to 22.2 pct K_2O , and recoveries from 84 to 99 pct. Sylvite flotation from chloride evaporites, with amine collector, recovered 90 to 97 pct of the potash in a concentrate containing 54.3 to 60.3 pct K_2O . Fatty acid flotation of the high-sulfate evaporite recovered 78 pct of the sulfate minerals in a 27.8-pct- K_2O concentrate. Flotation of the chloride minerals with amine collector recovered 80 pct of the potash in a 59.7-pct- K_2O concentrate.

Solar evaporation of 10,000 gal of brine recovered 99 pct of the potash in a crude evaporite containing 24.5 pct schoenite and 20 pct sylvite. Continuous flotation in a 100-lb/h process research unit recovered over 95 pct of the potash in schoenite and sylvite concentrates containing 28.0 and 62.3 pct K_2O , respectively. An economic evaluation suggested a rate of return of 3 pct for a new facility and 9 pct if the process is adapted to fit an existing plant.

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INTRODUCTION

Over 80 pct of U.S. potash production comes from evaporite deposits near Carlsbad, NM (1).⁴ Most potash products are concentrated by flotation, selective dissolution of the gangue minerals, or precipitation of the mineral from hot brine. The majority of sylvinite ores, mixtures of KCl and NaCl, mined in New Mexico, are processed in grinding, desliming, sylvite flotation, and drying circuits (1-2) to produce directly marketable KCl fertilizer. Some langbeinite ($2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$) is concentrated by dissolving the readily soluble halite and sylvite gangue minerals. A heavy-medium process is used to physically separate the minerals into sylvite and langbeinite concentrates (2). Langbeinite is directly marketable or can be chemically refined to recover K_2SO_4 fertilizer. Some carnallite and sylvinite ores, with abundant insoluble material in the sylvite grains, are processed by selectively dissolving the potassium minerals in a NaCl brine and desliming the brine. A pure sylvite product is precipitated by controlling brine composition and temperature (2).

Nearly all of the above methods generate potassium-rich brines. In addition, most potash operations bleed off brine to control magnesium and sulfate levels. Some potash producers operate gas- or oil-fired evaporators for crystallization of salts to recover potassium from these brines. Rising costs and limited availability of fossil fuels throughout the United States have stimulated interest in devising alternative, energy-saving methods for recovering potash from process and waste brines.

The Bureau of Mines investigated potash recovery from plant process and waste brines, using the energy-conserving methods of solar evaporation and froth flotation.

Factors such as temperature, wind velocity, and amount of precipitation affect brine evaporation rate, evaporite yield, and mineral composition. Variations in these factors may cause products from laboratory evaporation and solar pond evaporation to differ in (1) brine composition at harvest, (2) composition of evaporites, and (3) crystal size of evaporites.

Laboratory evaporite compositions should be similar to those expected in solar ponds (3-5); however, laboratory evaporation rates do not approximate solar pond rates because of the lack of exposure to sunlight, wind, and precipitation.

Several potassium minerals will crystallize out of the brine during evaporation. Of these minerals, sylvite (KCl), leonite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) and schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) are concentrated by established methods without potassium redissolution (6-8). Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$) usually require conversion to either sylvite or leonite and schoenite before potassium minerals can be concentrated (6, 9); however, kainite can be floated directly from ore (8). Leonite, schoenite, and kainite are chemically refined to produce marketable K_2SO_4 fertilizer. Standard commercial processes have limited application to crude evaporites because of their complex mineralization. Therefore, alternate beneficiation schemes were devised for these evaporites. This report describes (1) the laboratory evaporation of process and waste brines and subsequent flotation of potash values from the crude evaporites, (2) the solar evaporation of 10,000 gal of waste brine, and (3) the operation of a continuous 100-lb/h process research unit (PRU) designed to technically evaluate the flotation procedure. An economic evaluation of the solar evaporation-flotation technique is also given.

⁴Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

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LABORATORY-SCALE RESEARCH

Laboratory-scale research consisted of (1) monitoring brine evaporation under controlled conditions, in the absence of direct sunlight, and (2) investigating methods for beneficiating the various types of crude salts produced by evaporation.

EVAPORATION EXPERIMENTS

Description of Process and Waste Brines

Samples of brine were obtained from potash companies operating in the Carlsbad area: five process brine samples, four tailings brine samples, and one brackish mine water. Table 1 shows the chemical analysis of each of these brines. (The suffixes A, B, and C relate to different brines from the same producer.) Brines containing less than 1 pct sulfate were considered to be chloride brines; brines containing more than 1 pct

sulfate were classed as sulfate-chloride brines.

Laboratory Evaporation Procedure

Evaporation tests were conducted in 4-ft-diam, 10-in-deep stainless steel pans supported on a wooden frame to limit energy exchange with the laboratory floor. Electric fans were used to simulate wind across the brine surface. Figure 1 shows a typical laboratory evaporation system. The brine evaporation rate was determined by measuring the volume changes with a micrometer hook gauge. In addition, evaporation rates of pure water and brine were compared. Maximum and minimum daily temperatures of brine and air above the pans were measured. Air movement over the pans was periodically determined with an anemometer, and the relative humidity was determined with a sling psychrometer. Samples of brine and fresh salt crystals

TABLE 1. - Chemical analyses of brine samples

Brine type and sample	Description	Sp gr	Composition, pct		Chemical analysis, pct					
			Salts	Water	K ₂ O	Na	Mg	Ca	SO ₄	Cl
Cl brines:										
1.....	Process brine...	1.235	27.5	72.5	5.1	4.6	2.1	0.03	0.4	16.2
2.....	...do.....	1.234	28.6	71.4	5.9	6.9	.4	.06	.4	16
3.....	Brackish mine waste water.	1.128	17.5	82.5	1.8	4.8	.2	.22	1.0	9.9
4A.....	Tailings brine..	1.232	29.0	71.0	4.1	8.4	.4	.02	.8	16.7
SO ₄ -Cl brines:										
4B.....	...do.....	1.182	22.7	77.3	1.7	6.9	.5	.04	1.8	12
5A.....	...do.....	1.204	24.8	75.2	2.5	7.1	.4	.03	1.8	13.4
5B.....	...do.....	1.204	23.6	76.4	2.6	7.2	.4	ND	1.6	12.5
6A.....	Process brine...	1.257	29.7	70.3	5.1	5.0	2.1	ND	4.5	13.9
6B.....	...do.....	1.280	32.7	67.3	5.3	5.5	2.4	ND	4.8	15.8
6C.....	...do.....	1.272	30.7	69.3	4.7	5.2	2.4	ND	4.4	14.8

ND Not detected.



FIGURE 1. - Evaporation pans and monitoring equipment for potash brine evaporation studies.

were taken periodically for chemical and petrographic analyses.

Brine composition was plotted on a tertiary-phase diagram to monitor the progress of evaporite crystallization. Evaporation continued until 10 pct carnallite or kainite appeared in the fresh crystals. At the end of each test, evaporite salts were removed from the evaporation pan, drained of excess brine, and stored in plastic bags.

Evaporation Results and Discussion

Under laboratory test conditions, daily high and low air temperatures averaged 76° and 66° F, respectively. Average air movement across the evaporation pans was 1 mph. Table 2 shows the evaporation data for each brine sample. Laboratory evaporation rates, calculated on an annual basis, ranged from 14 to 34 in, or from approximately 40 to 95 pct of the water evaporation rate during the same

TABLE 2. - Laboratory evaporation test conditions

Brine sample	Average daily air temp, °F		Air velocity, mph	Initial brine volume, gal	Average daily brine temp, °F		Total days evaporation	Evaporation rate, ¹ in/yr
	High	Low			High	Low		
1.....	76	67	1.2	53	68	62	45	34
2.....	76	67	.9	56	68	63	109	19
3.....	75	67	.7	45	70	64	78	22
4A.....	75	63	.1	62	75	64	128	19
4B.....	76	68	1.0	31	71	63	54	22
5A.....	76	69	.9	35	70	67	61	22
5B.....	82	63	.1	58	74	64	144	15
6A.....	76	67	1.1	59	68	62	55	33
6B.....	75	63	.1	64	73	63	88	19
6C.....	75	63	.1	36	75	65	74	14

¹The comparable water evaporation rate under laboratory test conditions was 36 in/yr.

period. Solar evaporation in the Carlsbad, NM, area would be significantly greater. For example, a survey over a recent 8-yr period showed that the average daily high and low air temperatures during the evaporation season (April through October) were 87° and 58° F, respectively. Air movement averaged 8 mph, and brine evaporation rates varied from 81 to 85 in during the season (10).

Laboratory evaporite crystallization paths generally proceeded toward the carnallite field on a tertiary-phase diagram as shown in figures 2 and 3. Crystallization paths of the chloride brines (samples 1 and 2) started in the sylvite field and moved towards the carnallite field as sylvite and halite continually crystallized. The brackish mine waste water, which contained significant amounts of calcium and sulfate (sample 3), started in the glaserite ($\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$) field; however, the crystallization path proceeded into the sylvite field after the calcium and sulfate precipitated as gypsum. The path followed that of a typical chloride brine.

The crystallization paths of sulfate-chloride brines generally moved towards the carnallite field from the glaserite

field as schoenite, sylvite, and halite crystallized. As the path approached the kainite-leonite interface, some kainite and leonite were crystallized with the schoenite, sylvite, and halite.

Sample 4A (chloride brine) started in the sylvite field and initially acted like a chloride brine; however, as the sulfate content increased during evaporation, the path moved across the leonite-sylvite interface. The brine then behaved like a sulfate-chloride brine, crystallizing kainite, leonite, sylvite, and halite.

Between 84 and 99 pct of the potash was recovered in the evaporite salts. Chemical analyses of end brines and harvested evaporite salts are shown in table 3, and petrographic analyses of evaporite salts are shown in table 4. The evaporites contained 7.2 to 22.0 pct K_2O . Evaporite crystal size ranged from 4 to 35 mesh. Liberation size of the potassium minerals ranged from 28 to 35 mesh. Chloride brines (samples 1 to 4A) yielded evaporites containing 15 to 35 pct sylvite with less than 5 pct carnallite. Sulfate-chloride brines yielded a variety of mineral combinations. Sample 5A and 6A evaporites contained 5 and 20 pct

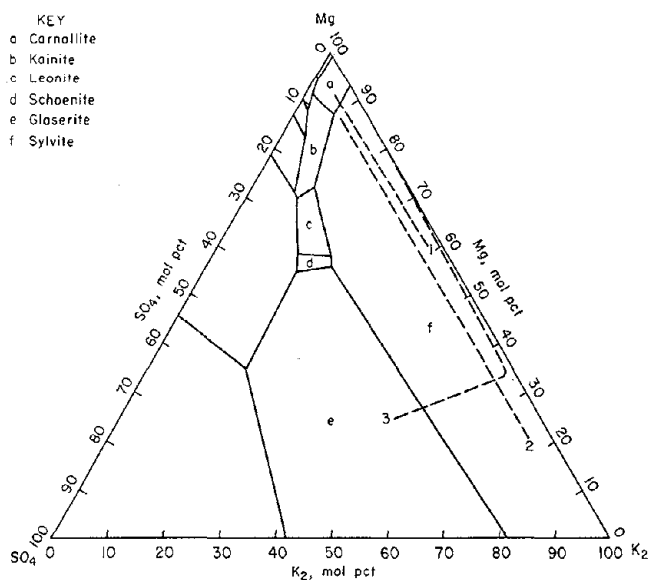


FIGURE 2. - Crystallization paths of chloride brines under laboratory evaporation conditions.

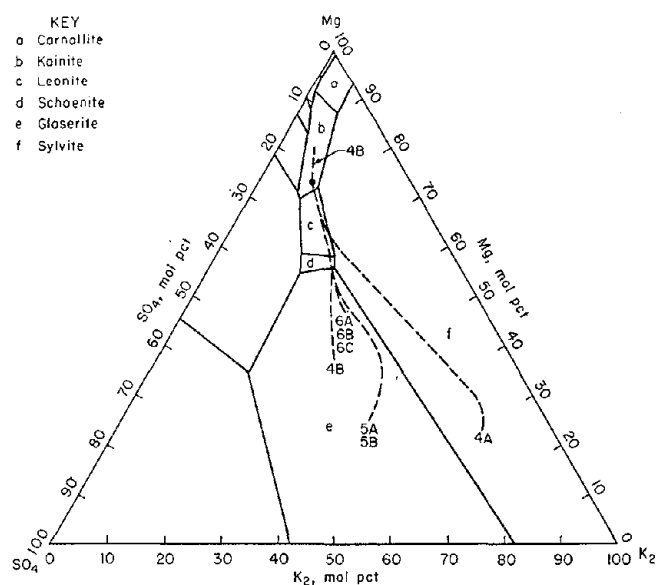


FIGURE 3. - Crystallization paths of sulfate and sulfate-chloride brines under laboratory evaporation conditions.

kainite, respectively. In four other evaporites (samples 4B, 5B, 6B, and 6C) only trace amounts of kainite were found,

but 5 to 20 pct schoenite and/or leonite were present.

TABLE 3. - Chemical analyses of laboratory evaporation products

Brine sample	Distribution, wt pct	K ₂ O recovery, pct	Sp gr	Chemical analysis, pct				
				K ₂ O	Na	Mg	SO ₄	Cl
END BRINE AT HARVEST								
1.....	55	9	1.289	1.7	0.7	6.6	1.1	20.9
2.....	12	1	1.287	2.4	1.1	6	1.6	17.3
3.....	27	11	1.252	3.6	2.6	3.6	<.1	19.3
4A.....	9	1	1.320	2	.8	7.2	4.7	19.3
4B.....	16	7	1.306	2.8	1.5	5.8	5.7	17.2
5A.....	5	1	1.330	1.8	.7	7.0	4.6	19.5
5B.....	18	7	1.300	3.1	2.6	5.1	5.6	16.5
6A.....	38	7	1.314	1.9	.8	6.3	4.2	18.6
6B.....	49	12	1.304	2.3	1.2	6	4.2	18.4
6C.....	54	16	1.311	2.8	1.4	6.4	5.8	18
HARVEST SALTS								
1.....	45	91	ND	22.2	22.6	0.2	0.5	51.3
2.....	88	99	ND	18.3	21.6	1.6	.9	52
3.....	73	89	ND	10.1	30.8	.5	1.1	51.4
4A.....	91	99	ND	14.8	26.9	.5	1.7	54.7
4B.....	84	93	ND	7.2	30.7	.9	6.4	49.7
5A.....	95	99	ND	10.2	28.8	1.1	2.7	49.8
5B.....	82	93	ND	9.6	30.8	.9	5.6	52.7
6A.....	62	93	ND	16.7	17.8	2.7	12.5	42.5
6B.....	51	88	ND	17.7	19.6	2.1	16.9	38
6C.....	46	84	ND	17.7	23.3	2.2	11	45.5

ND Not detected.

TABLE 4. - Petrographic analyses of evaporites

Evaporite samples	Chemical analysis, pct		Evaporite minerals, wt pct					Liberation size for potassium minerals, mesh	Other trace minerals
	K ₂ O	SO ₄	Syl-vite	Ha-lite	Carnall-ite	Kai-nite	Leonite and/or schoenite		
1.....	22.0	0.5	35	60	Trace	ND	ND	35	ND.
2.....	18.3	.9	30	60	5	Trace	ND	35	Glauberite, gypsum.
3.....	10.1	1.1	15	80	ND	Trace	Trace	35	Gypsum, glaserite.
4A.....	14.8	1.7	25	70	Trace	Trace	Trace	35	ND.
4B.....	7.2	6.4	5	80	ND	Trace	10	35	Glaserite, glauiberite.
5A.....	10.2	6.7	10	85	ND	5	ND	35	Glauberite.
5B.....	9.6	5.6	15	80	ND	Trace	5	28	Epsomite, glauiberite.
6A.....	16.7	12.5	20	50	ND	20	10	35	ND.
6B.....	17.7	16.9	25	55	Trace	ND	20	28	Epsomite.
6C.....	17.7	11.0	20	65	ND	Trace	15	28	Do.

ND Not detected.

BENEFICIATION OF CRUDE EVAPORITES

All beneficiation studies were conducted in saturated brine made from a portion of the respective evaporite. These process brines were similar in composition to the initial evaporation brines.

Grinding Studies

In preparation for beneficiation, the crude evaporites were crushed through 4-mesh size, and size distributions of the crushed evaporites were determined (fig. 4). Only 10 pct of the crushed material was finer than the 35-mesh liberation size; consequently, the evaporites were further ground to pass 35 mesh using two-stage grinding in a rod or ball mill. For the first stage, 1 kg of evaporite was ground in saturated brine at 50 pct solids. After screening at 35 mesh, the oversize was reground in a second stage at 50 pct solids. Two 6-min grinds with the ball mill or two 1-min grinds with the rod mill were required to grind 95 pct of the evaporite through 35-mesh

size. Size distribution of No. 2 brine evaporite feed and the ball and rod mill products are shown in figure 5. The rod mill was used in beneficiation test work because it produced a coarser product

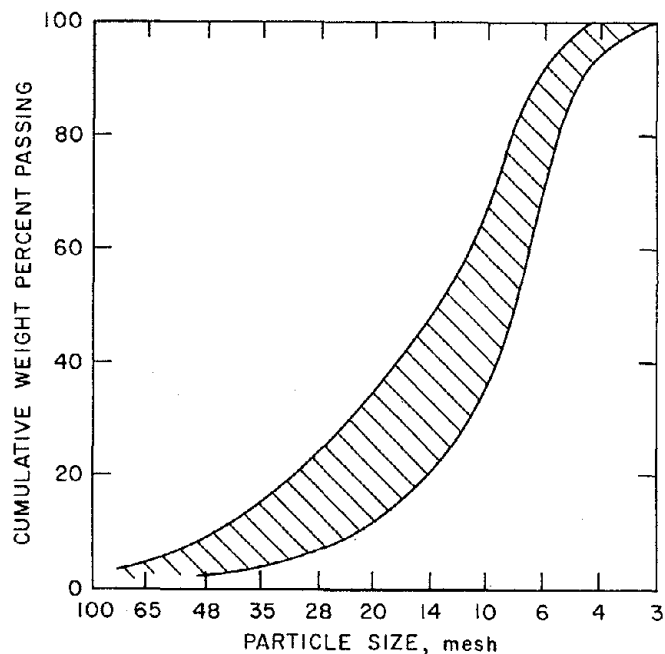


FIGURE 4. - Size distribution range of crushed evaporites from all brine harvests.

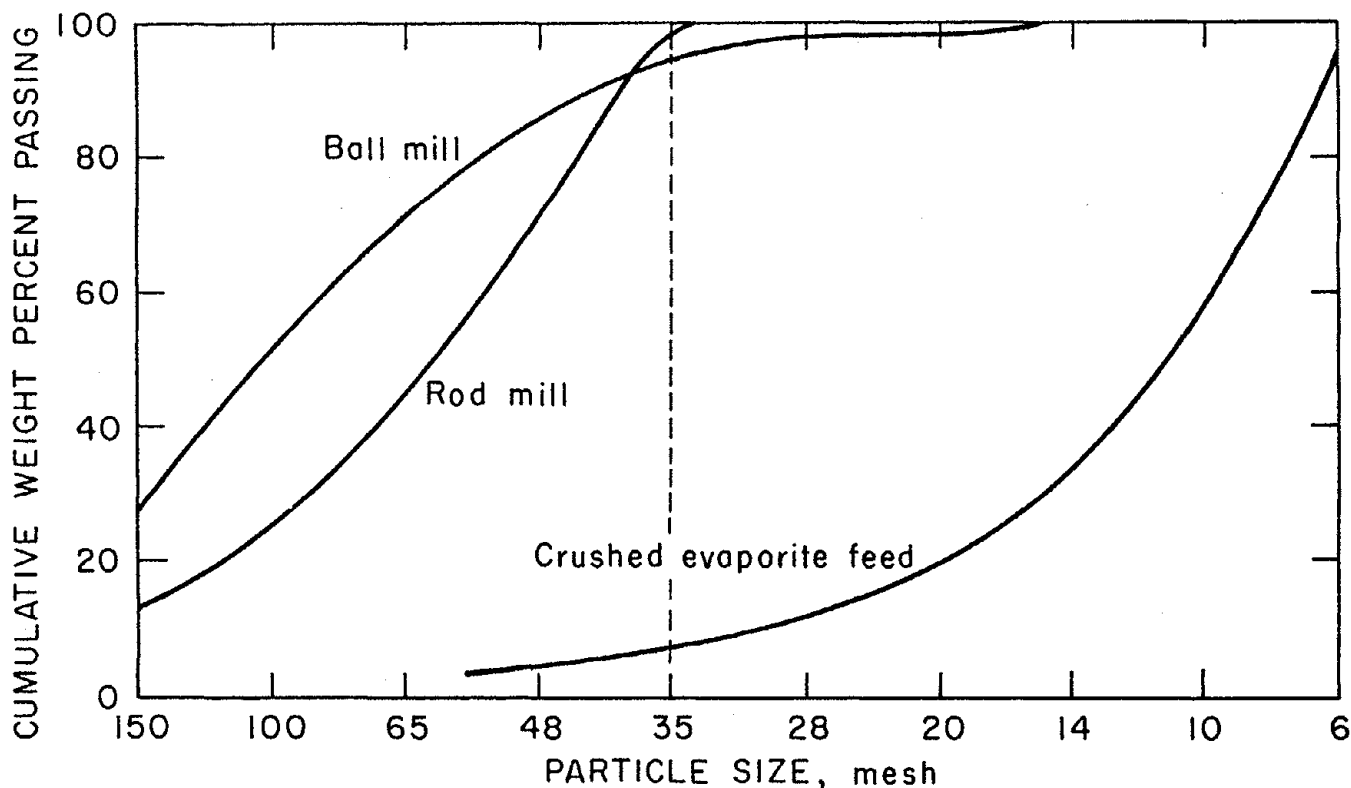


FIGURE 5. - Size distribution of No. 2 evaporite feed and ball and rod mill products.

than the ball mill. Petrographic and chemical analyses of ground evaporite showed potassium minerals uniformly distributed throughout the size fractions.

Flotation of Chloride Evaporites

Sylvite was floated from chloride evaporites using two-stage rougher flotation followed by a single stage of cleaning. A flow diagram for this method is shown in figure 6. Two series of tests were performed using this general procedure. One established optimum reagent dosage, and the other determined the reliability of the procedure under simulated continuous operation (locked-cycle flotation).

After grinding through 35-mesh size, the evaporite was pulped with saturated brine to 30 pct solids and placed in a 1,000-g laboratory flotation cell. The pulp was conditioned at a 13-ft/s peripheral impeller speed for 5 min with half the reagent dosage and floated for 2 min.

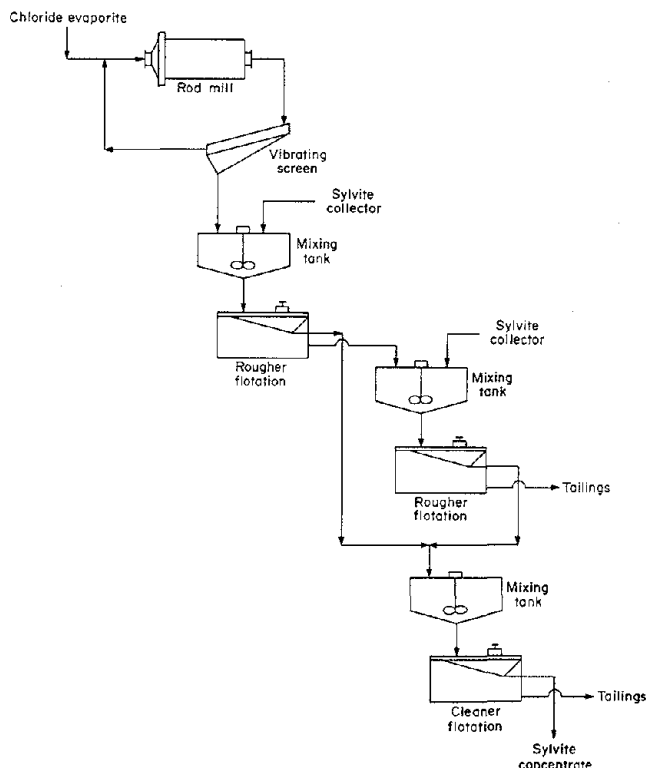


FIGURE 6. - Flowsheet for potash recovery from chloride evaporites.

This procedure was repeated using the second half of the collector dosage. Both rougher sylvite concentrates were combined and placed in a 500-g flotation cell. After a 1-min conditioning without additional reagents, the sylvite was re-floated for 2 min producing the cleaner sylvite flotation concentrate. The sylvite collector was an emulsion of 2 parts Armeen TD⁵ (a primary alphatic tallow amine neutralized with HCl), 1 part Barrett's oil, and 37 parts water. Collector emulsion dosage ranged from 0.05 to 0.4 lb/ton. Figure 7 shows the results for evaporites 1, 2, 3, and 4A.

⁵Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

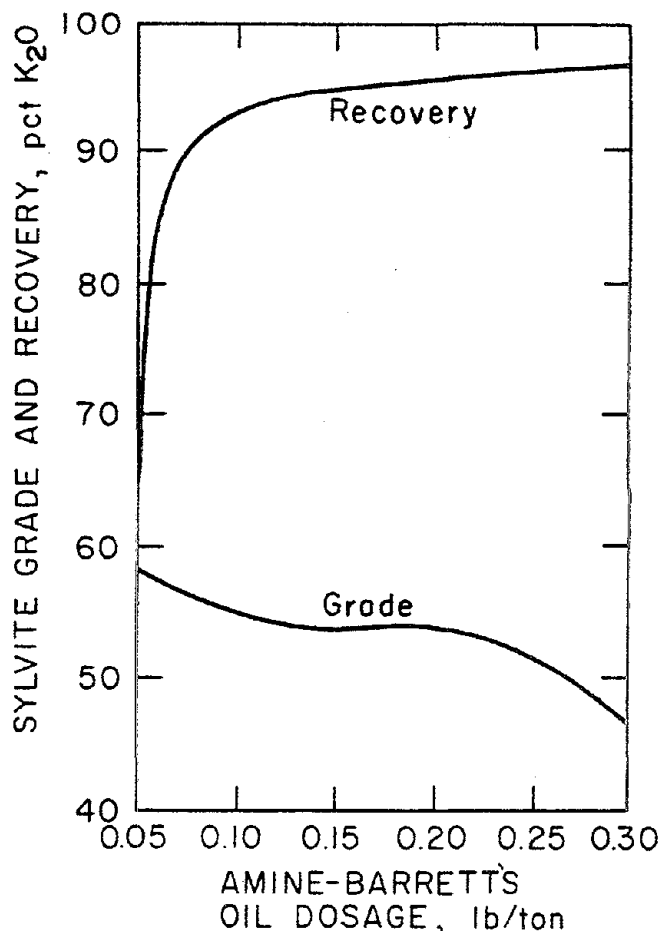


FIGURE 7. - Effect of amine-Barrett's oil dosage on sylvite cleaner flotation response for chloride evaporites.

Potash recoveries increased with greater reagent dosages while grades decreased. Optimum collector dosage was 0.2 lb/ton for all four chloride evaporites. At this dosage, flotation recovered 95 pct of the potash at a cleaner concentrate grade above 50 pct K_2O .

Locked-cycle flotation tests were conducted to simulate a continuous operation. The flotation procedure was similar to that described above, with 0.1 lb/ton of collector added to each of the two rougher flotation stages. For each flotation cycle, the cleaner tailings were combined with the flotation feed for the next cycle. After four to five cycles, the test was terminated when the weight of the recycled cleaner flotation tailings was stabilized. Locked-cycle flotation results for the chloride brine evaporites are shown in table 5. From 90 to 97 pct of the potash was recovered in the steady-state cleaner concentrates containing 54.3 to 60.3 pct K_2O . Subsequent recleaner flotation without reagents, followed by a fresh water spray leach with one part water to four parts recleaner concentrate, upgraded the recleaner concentrates to a range of 58.2 to 62.5 pct K_2O . Based on K_2O content of the recleaner concentrate, the recoveries averaged 94 pct. Size analysis of the final products showed that over 80 wt pct of the potash was plus 150 mesh. The final potash concentrate grade would be suitable for the fertilizer market; however, compaction may be necessary to produce a more desirable product size.

Flotation of Sulfate-Chloride Evaporites

Three types of evaporites, high-sulfate, low-sulfate, and kainite-bearing, were beneficiated by flotation to recover

the potash values. The generalized flotation procedure is illustrated in figure 8. The procedure consisted of (1) kainite conversion to leonite or schoenite, (2) grinding to liberation size, (3) leonite-schoenite rougher and cleaner flotation using caprylic acid collector, and (4) sylvite rougher and cleaner flotation using amine-Barrett's oil collector. The kainite conversion step was deleted when testing the high-sulfate and low-sulfate evaporites. Liberation size was 28 mesh for the high- and low-sulfate evaporites and 35 mesh for the kainite-bearing evaporites.

High-Sulfate Evaporites

The high-sulfate evaporites, samples 6B and 6C, containing 20 and 15 pct schoenite, 25 and 20 pct sylvite, and 55 and 65 pct halite, respectively, were blended for flotation testing. This composite flotation feed contained 18.8 pct K_2O , 20.6 pct Na, 2.82 pct Mg, 14.1 pct SO_4 , and 41.5 pct Cl.

Optimization results for schoenite flotation reagent are shown in figure 9. Best flotation occurred using a total reagent addition of 0.4 lb/ton of caprylic acid. Over 65 pct of the schoenite was recovered in a rougher concentrate at a grade of 61 pct schoenite. The total K_2O content was 22.3 pct of which 12 pct was sylvite, which floated with the schoenite. The optimum reagent dosage for sylvite flotation (fig. 10) was 0.2 lb/ton of amine-Barrett's oil emulsion. Because a portion of the sylvite reported to the schoenite concentrate, only 86 pct of the sylvite was recovered in a sylvite concentrate containing 68 pct sylvite. The total K_2O content was 45 pct.

TABLE 5. - Locked-cycle flotation results for chloride evaporites

Evaporite sample	Number of cycles	Cleaner sylvite concentrate, pct K_2O	Rougher tailings, pct K_2O	K_2O recovery, pct
1.....	5	55.1	1.0	96
2.....	5	54.3	1.0	97
3.....	4	58.4	1.2	90
4A.....	4	60.3	1.1	96

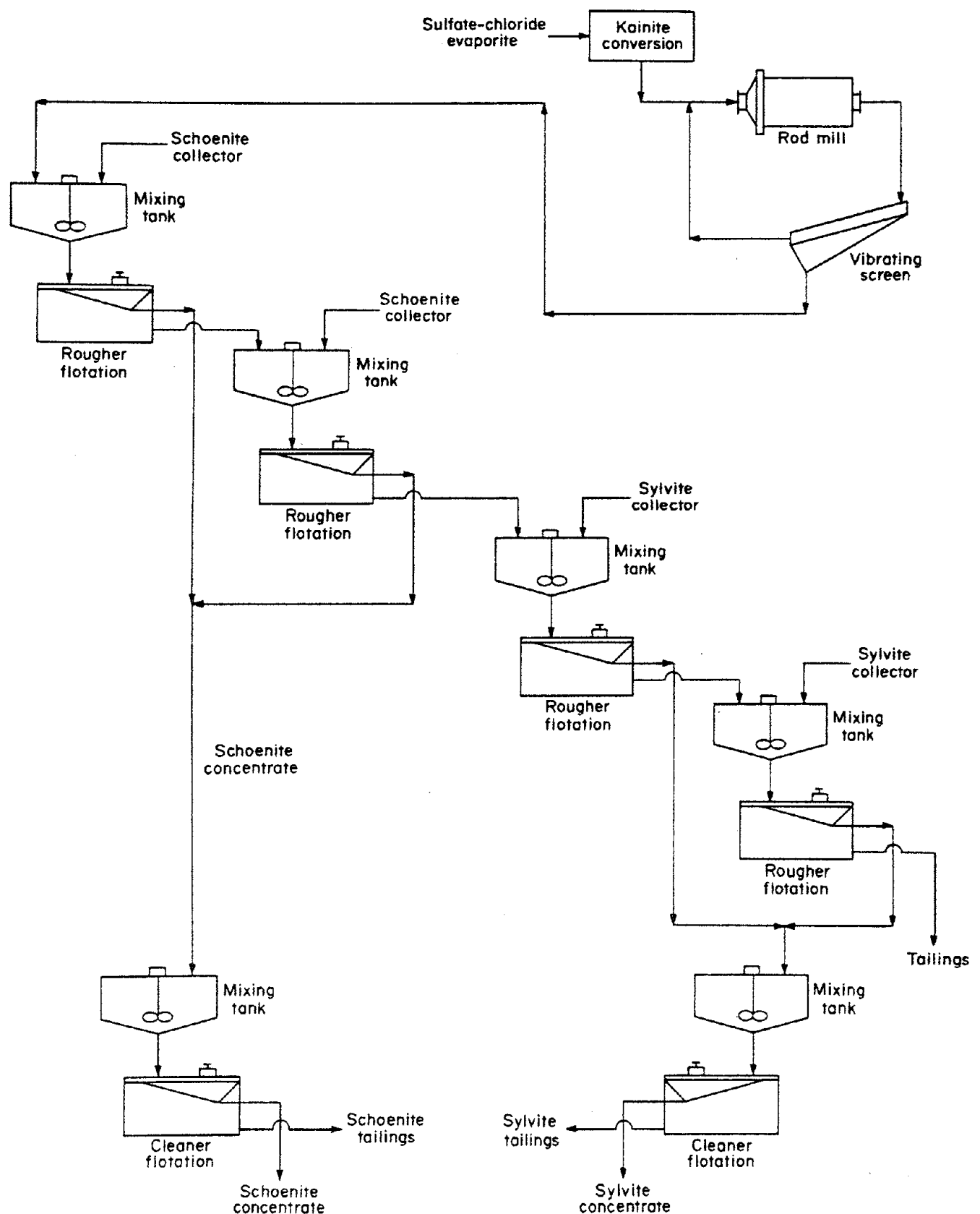


FIGURE 8. • Flowsheet for recovery of potash from sulfate-chloride evaporites, including the kainite conversion step.

In separate operations, schoenite and sylvite rougher concentrates were reconditioned without additional reagents and refloated to produce schoenite and sylvite cleaner concentrates. Cleaner flotation recovered 78 pct of the schoenite in a concentrate of 27.8 pct K_2O . The sylvite was not completely rejected during cleaner flotation, accounting for the high concentrate grade. The sylvite cleaner concentrate contained 82 pct of the sylvite at a 55-pct- K_2O grade. Subsequent sylvite recleaner flotation

without reagents and a spray water leach with one part water to four parts recleaner concentrate produced a 59.7-pct K_2O grade concentrate. Final sylvite recovery was 80 pct.

Locked-cycle flotation tests, simulating a continuous flotation operation, were conducted to determine the effect of middling product and brine recycle on potash flotation and to obtain data for process scale-up. Flotation reagent dosages were 0.4 lb/ton of caprylic acid and 0.2 lb/ton of amine-Barrett's oil emulsion. The dosages were divided equally between rougher schoenite and sylvite stages, respectively. As shown in figure 11, schoenite and sylvite cleaner tailings were recycled back to their corresponding rougher flotation circuits. Brine was recycled as completely as possible. New brine was added only to replace brine lost in the filter cakes during mechanical handling.

Locked-cycle flotation results for the high-sulfate evaporite (6B-6C) are shown in table 6. Five complete cycles were made to ensure steady state. Potash recovery was 96 pct in a schoenite cleaner concentrate containing 28.4 pct K_2O and a sylvite cleaner concentrate containing

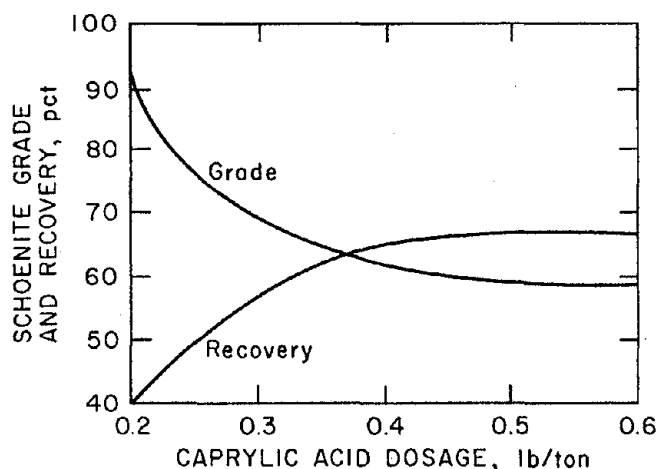


FIGURE 9. - Effect of caprylic acid dosage on schoenite rougher flotation response for high-sulfate evaporites.

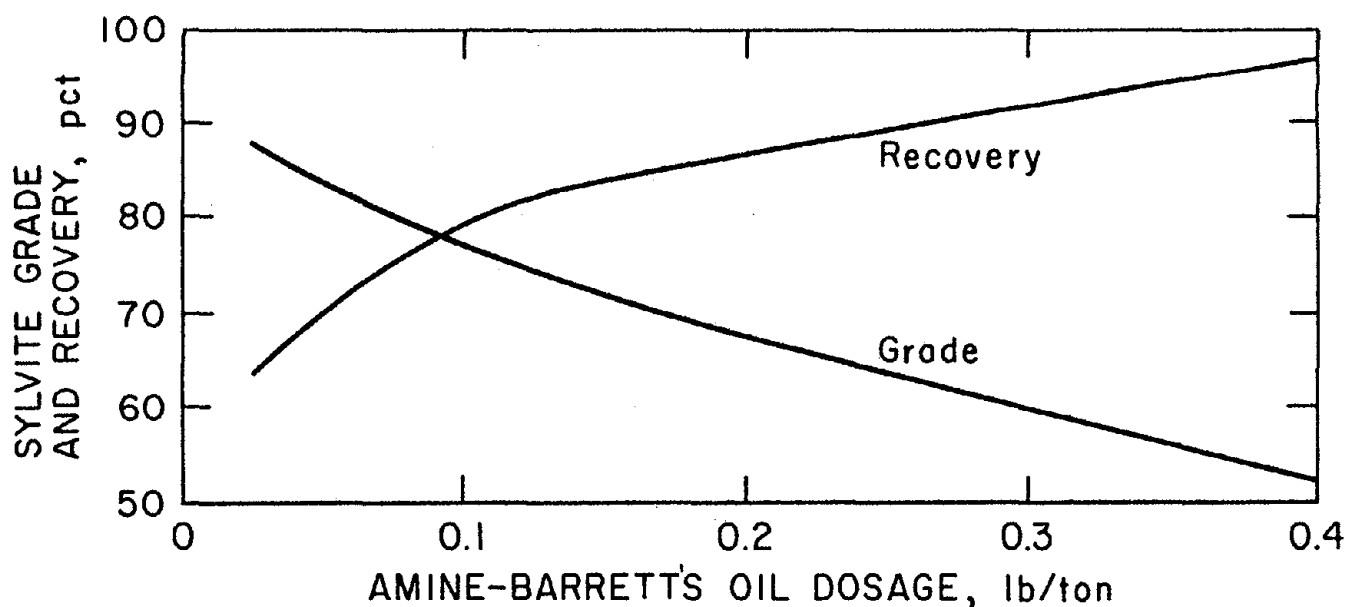


FIGURE 10. - Effect of amine-Barrett's oil dosage on sylvite rougher flotation response for high-sulfate evaporites (6B-6C).

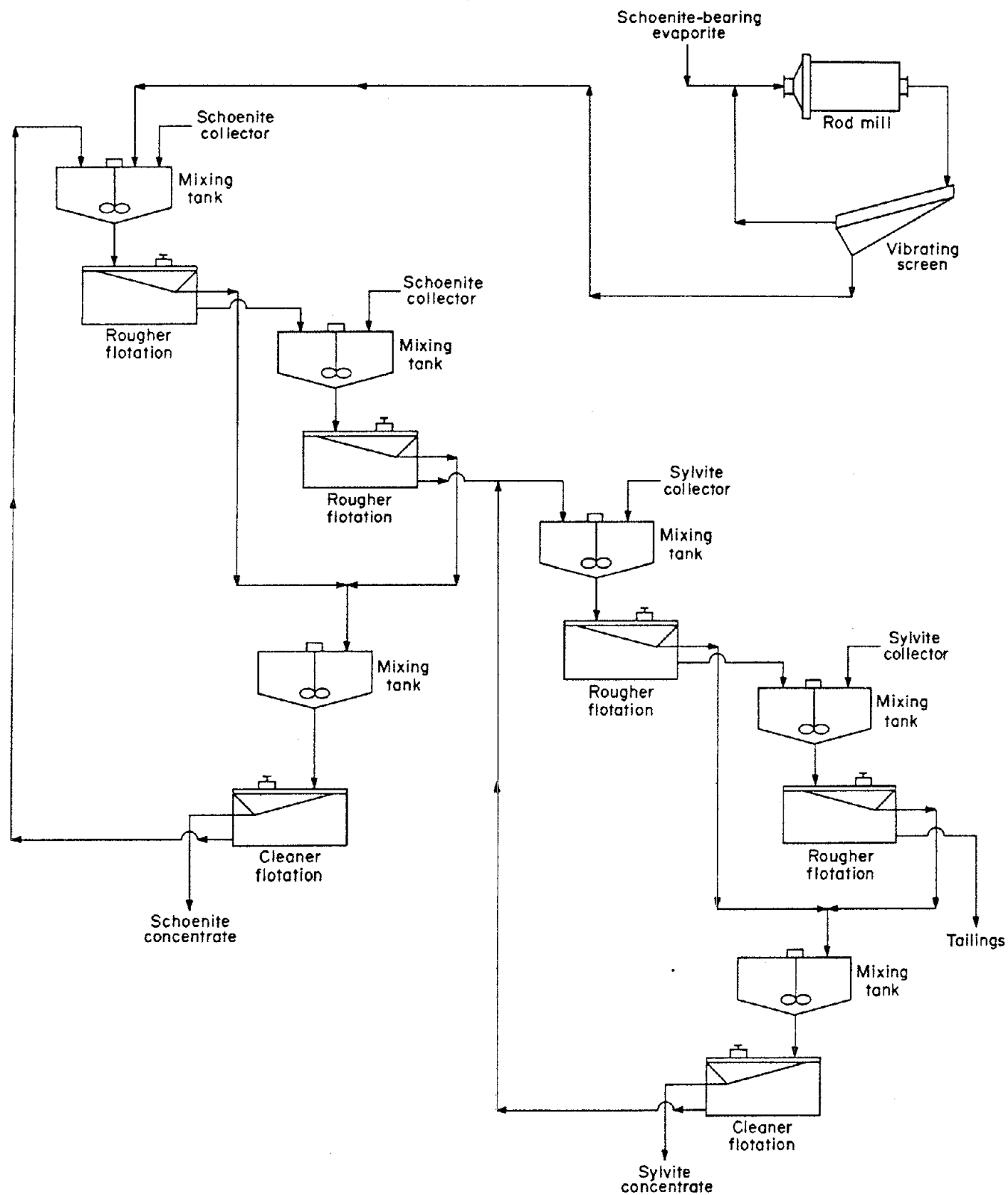


FIGURE 11. • Locked-cycle test flowsheet for recovery of potash from schoenite-bearing evaporites.

TABLE 6. - Locked-cycle flotation results for high-sulfate evaporite (composite 6B and 6C), percent

Product	K ₂ O grade	Schoenite recovery	Sylvite recovery
Schoenite cleaner concentrate	28.4	66	30
Sylvite cleaner concentrate..	47.4	33	67
Final tailings.....	1.2	1	3

47.4 pct K₂O. Thirty percent of the sylvite was recovered in the schoenite concentrate, and 33 pct of the schoenite was recovered in the sylvite concentrate.

Compared with the concentrate resulting from batch flotation, the locked-cycle schoenite concentrate had a higher schoenite grade because more sylvite appeared in it. This was attributed to reagent buildup in the recycled brine, which resulted in bulk flotation of both schoenite and sylvite. Subsequent to this test series, laboratory experiments showed that the organic reagents are effectively removed by passing the brine through activated carbon.

Low-Sulfate Evaporites

Of the low-sulfate evaporites (samples 4B and 5B), only sample 5B, containing 5 pct schoenite, 15 pct sylvite, and 80 pct halite, was used in flotation testing.

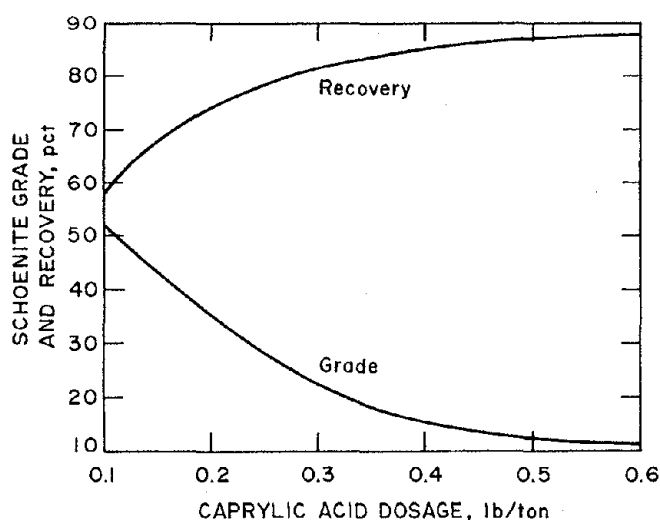


FIGURE 12. - Effect of caprylic acid dosage on schoenite rougher flotation response for low-sulfate evaporites.

Sample 4B was too low in potash content to warrant further testing. The flotation procedure used on sample 5B was similar to that used on high-sulfate evaporites.

Flotation test results are shown in figure 12. Optimum results were obtained using 0.2 lb/ton of caprylic acid. Over 74 pct of the schoenite was recovered in a rougher concentrate containing 34 pct schoenite. Optimum sylvite flotation (fig. 13) required 0.2 lb/ton of amine-Barrett's oil emulsion. Because 28 pct of the sylvite was in the schoenite concentrate, only 66 pct of the sylvite was recovered in a rougher concentrate. Cleaner flotation increased the sylvite grade to 53.4 pct K₂O at a recovery of 63 pct.

Because of the low (5 pct) schoenite content, the sample was treated as a chloride evaporite to recover the sylvite. Locked-cycle tests were conducted using 0.2 lb/ton of amine-Barrett's oil emulsion. After five complete cycles, over 97 pct of the potash was recovered in a cleaner concentrate containing 56 pct K₂O. Recleaner flotation followed

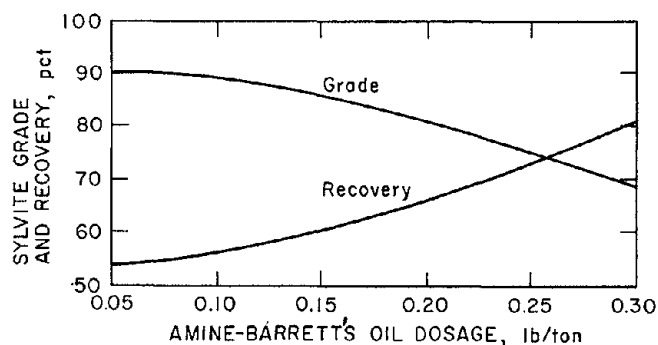


FIGURE 13. - Effect of amine-Barrett's oil dosage on rougher sylvite flotation response for low-sulfate evaporites.

by a fresh water spray leach produced a 59.8-pct-K₂O concentrate at 96 pct overall potash recovery.

Kainite-Bearing Evaporites

Samples 5A and 6A were kainite-bearing evaporites; however, only sample 6A, which had a higher kainite content, was selected for flotation investigations. It contained 20 pct kainite, 10 pct leonite, 20 pct sylvite, and 50 pct halite.

The flotation procedure was the same as that for the high-sulfate evaporite (see figure 8), except a kainite conversion step was necessary prior to flotation. Caprylic acid and amine-Barrett's oil emulsion at 0.2-lb/ton dosages were used as schoenite and sylvite collectors, respectively.

The literature reports several kainite conversion methods (6, 8). Three methods were investigated, using an equilibrium brine containing less than 3 pct magnesium to convert the kainite to leonite or schoenite. The first method (60-min agitation) involved mixing the low-magnesium brine and the evaporite at 28 pct solids for 60 min in a conditioner with a peripheral impeller speed of 9 ft/s. The second method (agitation-aeration) involved bubbling air through the 28-pct-solids slurry for 40 min. The third method (7-day static) involved allowing a 44-pct-solids mixture of the low-magnesium brine and the evaporite to remain undisturbed for 7 days.

To determine the effect each method had on subsequent schoenite flotation, a simple two-stage rougher flotation test on evaporite 6A was conducted using 0.2 lb/ton of caprylic acid. Test results listed in table 7 showed that--

- Without kainite conversion, rougher flotation recovered only 54 pct of the total potash present as the sulfate-type minerals kainite and schoenite.

- The 60-min agitation method (without air) converted kainite to leonite and

TABLE 7. - Comparative results of a simple two-stage schoenite rougher flotation on kainite-bearing evaporites with and without kainite conversion step

Kainite conversion method	Analysis, pct K ₂ O	Schoenite recovery, pct
Without conversion.	24.3	54
60-min agitation...	24.6	57
Agitation-aeration.	26.7	95
7-day static.....	25.0	85

schoenite, but flotation recovered only 57 pct of the total potash present as sulfate-type minerals.

- The 40-min agitation-aeration method converted the kainite and the leonite to schoenite, and flotation recovered 95 pct of the schoenite.

- The 7-day static method converted the kainite to leonite and schoenite, and flotation recovered 85 pct of the total potash present as sulfate-type minerals.

Although the agitation-aeration test results were the best, the 7-day static conversion method was an effective alternative as it did not require mechanical energy.

Following schoenite flotation, the schoenite tailings of both the agitation-aeration and 7-day static methods were refloated using 0.2 lb/ton of the amine-Barrett's oil emulsion to recover the sylvite. Sylvite recoveries in the cleaner concentrates were 83 and 86 pct, and the grades were 58.7 and 54.9 pct K₂O, respectively. From 11 to 12 pct of the sylvite was recovered in the schoenite concentrate. This accounts for lower potash recoveries in the sylvite concentrate and higher potash grades in the schoenite concentrates. The overall potash recoveries were 99 and 94 pct for the agitation-aeration and 7-day static methods, respectively.

The brine composition changed during the kainite conversion. The brine

composition change and the salt minerals present at a given time are illustrated in figures 14 and 15. When kainite was converted by the agitation-aeration method (fig. 14), the magnesium and sulfate

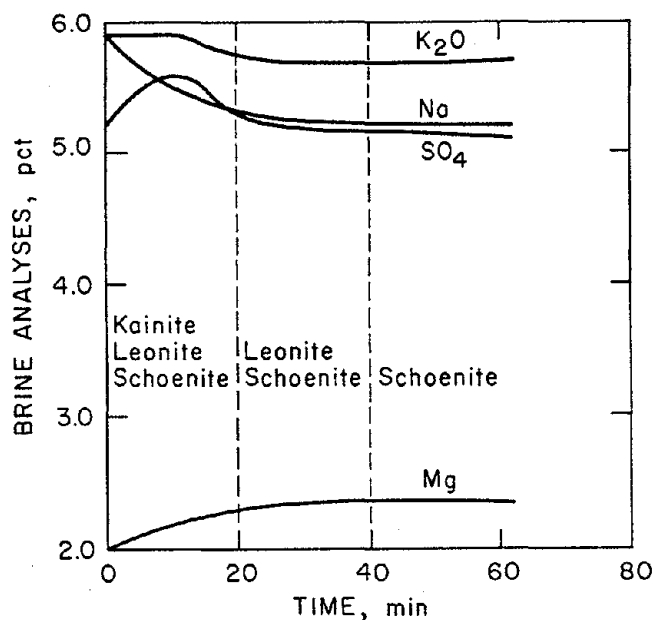


FIGURE 14. - Brine analyses and minerals present during agitation-aeration conversion of kainite (28 pct solids) in harvest 6A.

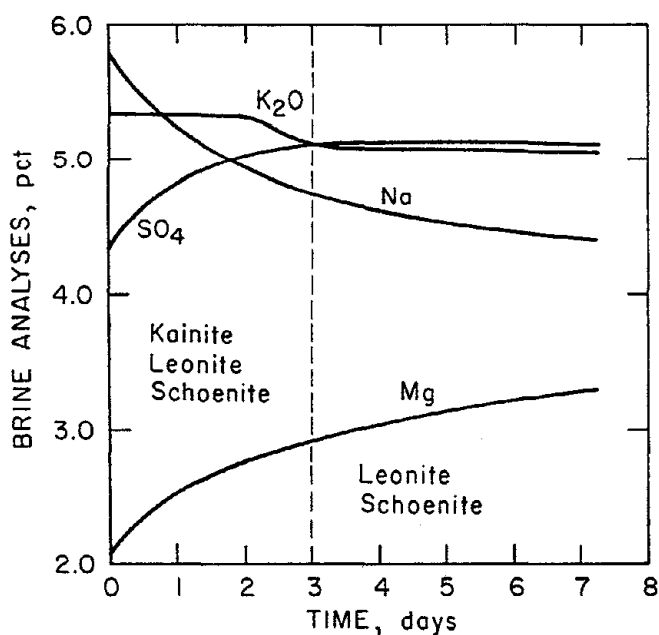


FIGURE 15. - Brine analyses and minerals present during 7-day static conversion of kainite in harvest 6A.

content of the brine increased initially while the potassium and sodium content decreased. After kainite was converted to schoenite, the magnesium content continued to increase slightly, while sodium and sulfate content decreased slightly; the potassium concentration essentially remained constant. Although not shown, the brine composition changed similarly when kainite was converted by the agitation method; however, complete conversion to schoenite was not achieved.

During conversion by the 7-day static method, the magnesium and sulfate content of the brine increased steadily, while sodium and potassium content decreased. Complete conversion was not achieved.

The initial magnesium concentration also had an effect upon the subsequent schoenite flotation. Figure 16 shows how the flotation recovery decreased as the initial magnesium content of the brine

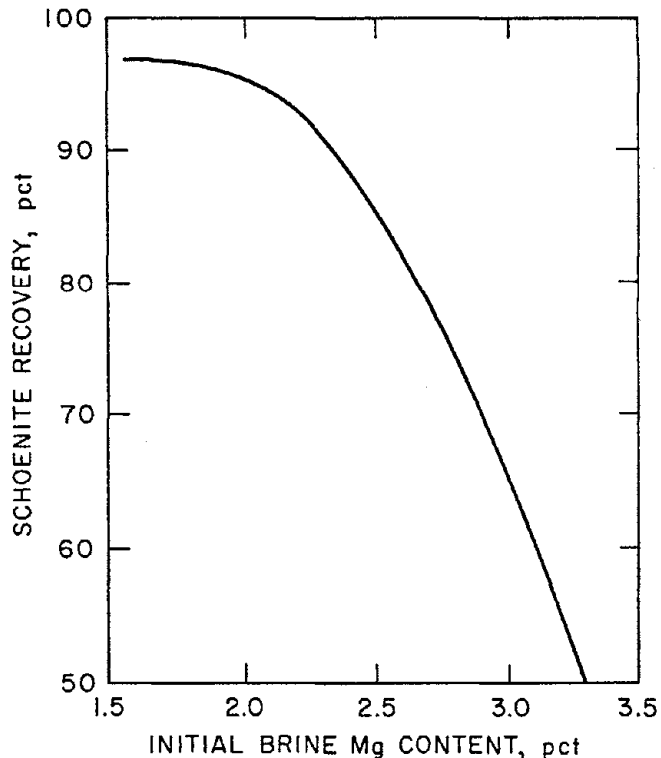


FIGURE 16. - Effect of initial magnesium content of brine on schoenite flotation recovery from sulfate-chloride evaporites.

increased above 2.2 pct. In a continuous process, the magnesium content of the brine would gradually increase. To keep the content around 2 pct, the high-magnesium brine must be replaced with fresh brine or diluted with a magnesium-free brine. In both cases, potassium from the evaporite will be dissolved, resulting in a net potash loss to the brine.

To achieve maximum potash recovery, solar evaporites should not contain significant amounts of kainite. Test results showed 13 to 20 pct of the potash in the harvested evaporites was used to

resaturate brine during kainite conversion; therefore, the overall recovery of potash from the kainite-bearing evaporite (sample 6A) was reduced to between 74 and 81 pct depending on the conversion method used. With kainite-free evaporites, samples 6B and 6C, the overall recoveries of potash from the pans were 88 and 84 pct, respectively.

Most of the potash dissolved during brine resaturation in the kainite conversion should be recoverable by evaporating the excess brine in solar ponds. This was not within the scope of current research.

SOLAR EVAPORATION-FLOTATION EVALUATION

To evaluate the evaporation and flotation of potash values from process and waste brines, solar ponds and a flotation process research unit (PRU) were constructed to simulate a continuous full-scale operation. The data generated were used to provide engineering data needed for technical and economical evaluation.

SOLAR EVAPORATION

Brine Analysis

A 10,000-gal brine sample from a Carlsbad, NM, potash company was obtained for evaporation in solar ponds to produce sufficient feed for a continuous PRU. Initial chemical composition of this brine is shown in table 8. The specific gravity of the brine was 1.260 g/cm³.

Pond Design

The solar evaporation ponds were constructed on property adjacent to the Bureau's Salt Lake City Research Center. The ponds had base dimensions of 20 by 20 ft and top dimensions of 24 by 24 ft, with a depth of 2 ft. The ponds were lined with 40-mil polyethylene-reinforced hypalon. Hypalon was used to avoid deterioration of the liners by sunlight. The pond was filled with brine to a depth of 10 in.

TABLE 8.- Initial chemical composition of solar pond brine

<u>Component</u>	<u>wt pct</u>
K ₂ O.....	5.9
Na.....	5.9
Mg.....	2.2
Ca.....	.003
SO ₄	15.4
Cl.....	15.7

The evaporite formed a bed approximately 4 in thick. The salt bed did not adhere to the pond liner; consequently, it fractured easily. The evaporites were harvested by breaking the salt and removing it to the sides of the ponds, allowing any brine to drain back to the pond. The harvest was then crushed and blended to ensure a representative feed for flotation in the PRU.

Solar Evaporation Results

The solar ponds were monitored for brine composition, evaporite composition, brine temperature, and air movement across the ponds throughout the evaporation. Brine composition was plotted on a tertiary-phase diagram (fig. 17). The initial brine was in equilibrium in the glaserite field. As the salt crystallized, the brine path moved through the

schoenite and leonite fields until reaching the harvest point in the kainite field. The decision to harvest the salts after 70 days of evaporation was based on brine composition and the amount of carnallite present in the freshly precipitated salts. Of the 10,000 gal of brine, approximately 600 gal were left after crystallization. The end brine, shown in table 9, contained only 0.39 pct K. In excess of 99 pct of the potassium was crystallized from the brine during evaporation. Approximately 15 tons of evaporite were produced in the ponds. The mineral composition, listed in table 10, shows the evaporite to contain 24.5 pct schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) and 20 pct sylvite (KCl). Petrographic examination indicated that the sylvite and schoenite were liberated at 35 mesh.

TABLE 9. - Solar pond end brine composition

<u>Component</u>	<u>wt pct</u>
K ₂ O.....	0.47
Na.....	.29
Mg.....	7.28
Ca.....	.001
SO ₄	3.64
Cl.....	18.1

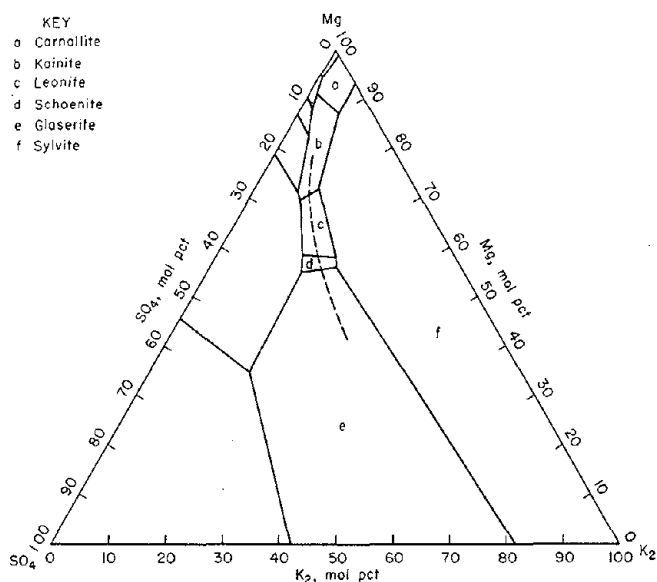


FIGURE 17. - Crystallization path of 10,000-gal brine sample in a solar evaporation pond.

TABLE 10. - Mineral composition of pond evaporite

<u>Mineral</u>	<u>wt pct</u>
Schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$).....	24.5
Sylvite (KCl).....	20.0
Halite (NaCl).....	51.5
Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$).....	3.0
Other.....	1.0

PRU DESIGN AND OPERATION

PRU design was based on data obtained from bench-scale, locked-cycle testing. The flow diagram presented in appendix figures A-1 through A-6 was adopted to recover schoenite and sylvite from the evaporite. The PRU is shown in figure 18.

Evaporite Preparation

Minus 3/8-in evaporite was fed to a 35-mesh vibrating screen. The plus 35-mesh screen fraction was sent to a rod mill and wet-ground at 50-pct-solids pulp density to minus 35-mesh in an equilibrium brine containing, in weight percent, 4.0 K, 4.5 Na, 3.0 Mg, and 5.5 SO₄. The minus 35-mesh screen fraction was mixed with the rod mill discharge and additional brine to form a 27-pct-solids slurry, which was pumped to the schoenite flotation section.

Schoenite Flotation

Slurry from the evaporite preparation section was fed to a conditioning tank and conditioned for 2 min with the schoenite collector, caprylic acid. The pulp flowed to two flotation machines,⁶ where the schoenite was floated for 7 min. The underflow from these cells was pumped to the sylvite flotation section. Froth from the schoenite rougher flotation cells flowed to a cleaner flotation cell where it was floated for 3.5 min and then recleaned for 3.5 min in another flotation cell. Underflow from both these

⁶All flotation cells in the PRU were Denver No. 5, sub A.

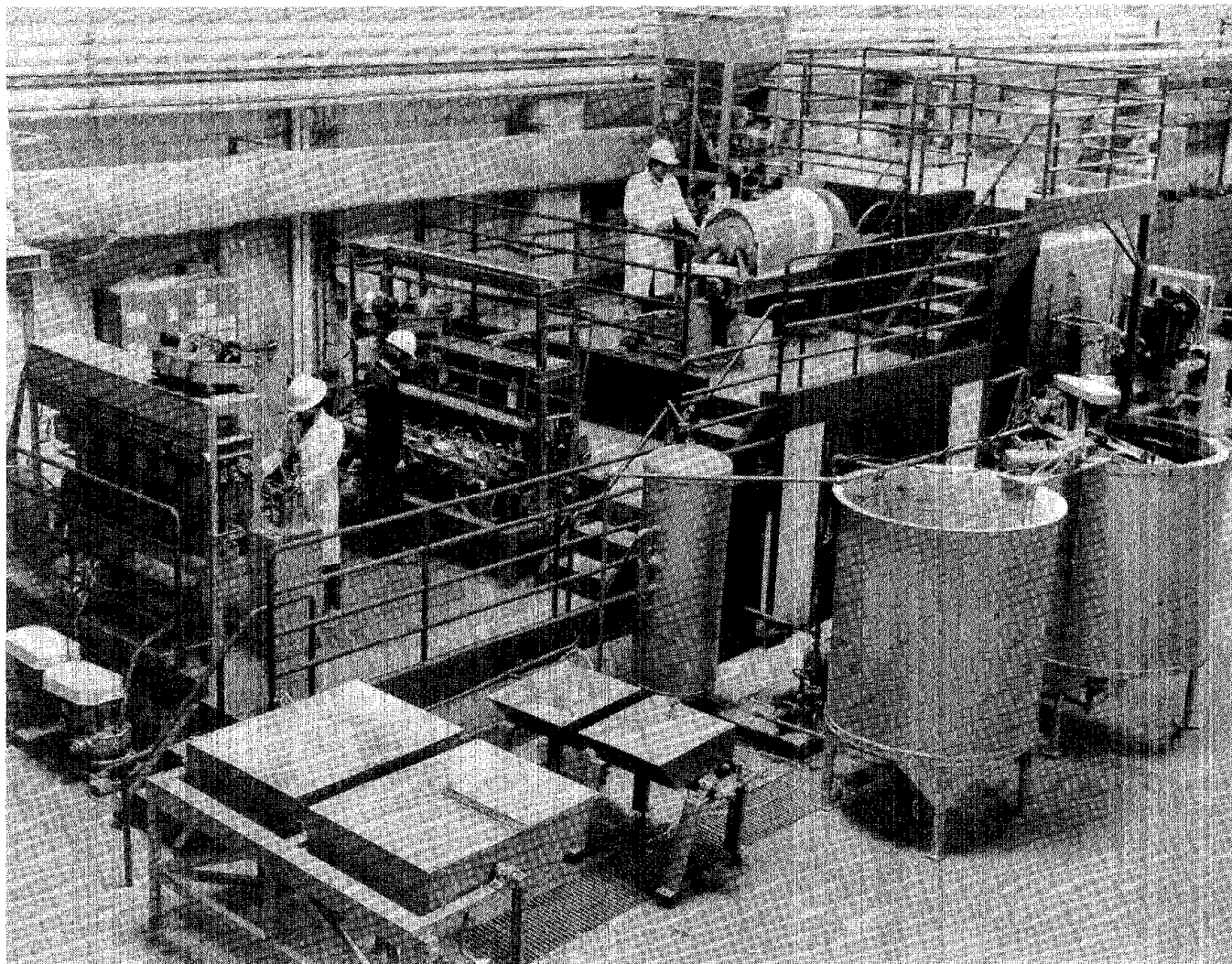


FIGURE 18. - Process research unit overview.

cells was recycled to the rougher flotation cells. Schoenite-rich froth from the recleaner flotation cell was pumped to the schoenite debrining section.

Sylvite Flotation

Pulp from the schoenite flotation section (underflow from rougher flotation) was fed to a conditioning tank and agitated for 2 min with an emulsion of Armeen TD amine and Barrett's oil. The pulp flowed to two rougher flotation cells where the sylvite was floated for 7 min. Underflow from these cells, containing halite and termed "salt tails," was pumped to the tailings debrining section. The sylvite rougher concentrate

was cleaned for 3.5 min in a flotation cell and recleaned for 3.5 min in another flotation cell. Underflow from sylvite cleaner and recleaner flotation was collected and recycled to rougher flotation. The sylvite recleaner concentrate was pumped to the sylvite debrining section.

Sylvite Concentrate Leaching

The sylvite recleaner concentrate was washed with water to remove fine halite entrained in the froth and to increase the product grade in excess of 60 pct K_2O , producing a marketable product. Potash losses during the final product leaching were less than 0.7 pct.

Product Debrining and Brine Recycle

Schoenite and sylvite concentrates and salt tailings were debrined in the PRU using pan filters for convenience.

The brine was pumped to a recycle brine tank. This tank served as a surge tank for process brine, which was metered to various points in the PRU. Excess reagents were removed by contacting the brine with activated carbon. The brine was filtered prior to recycling.

Operation

The reagent scheme (table 11) represents the optimum as determined by the PRU operation and is expressed as pounds of reagent per short ton of ore.

The data were collected during 12-h operations, with the exception of one continuous 96-h run.

TABLE 11. - Optimum flotation reagent addition

<u>Reagent</u>	<u>lb/ton</u>
Sylvite flotation: amine-	
Barrett's oil emulsion.....	0.2
Schoenite flotation: caprylic acid.....	.2

The main problems encountered were (1) the production of minus 100-mesh fines, which would require compaction of the final products, (2) the necessity of thoroughly cleaning the recycled brine to prevent contamination of sylvite in the

schoenite product, and (3) fine halite reporting to the sylvite concentrate.

During operation of the PRU, samples of plant feed, rod mill overflow, schoenite recleaner concentrate, sylvite feed, sylvite recleaner concentrate, salt tailings, and recycle brine were taken every 4 h for a complete material balance. The samples were filtered, dried, and assayed for potassium, sodium, magnesium, and sulfate.

Complete mass balances of potassium and sodium were made using simultaneous equations. The mass balances are shown in the appendix, figures A-1 through A-6.

Experimental Results

Results of the PRU operation are shown in table 12. These are optimum results under the reagents conditions listed in table 11. Based on flotation feed assay, 42 and 53.3 pct of the potassium was recovered in the schoenite and sylvite concentrates, respectively. The final schoenite and sylvite concentrates contained 28 and 62.3 pct K₂O, respectively.

A marketable sylvite product was produced; however, schoenite would have to be converted to K₂SO₄ to produce a marketable sulfate product. The schoenite-rich filter cake from the schoenite flotation circuit was dissolved in water, then heated to 122° F (50° C). At this temperature, the potassium sulfate crystallized while most of the magnesium impurities remained in solution. Nearly 59 pct of the potassium fed to the

TABLE 12. - Optimum flotation results of PRU for recovery of schoenite and sylvite from mixed-salt evaporite

Product	Evaporite grade, wt pct		Distribution, pct	
	K ₂ O	Na	K ₂ O	Na
Schoenite concentrate.....	28.0	8.1	42.0	11.8
Sylvite concentrate.....	62.3	1.3	53.3	1.1
Salt tailings.....	1.3	28.1	4.0	84.4
To brine (during sylvite leach)	Nap	Nap	.7	2.7

Nap Not applicable.

crystallizer was recovered in a K_2SO_4 concentrate containing 50.4 pct K_2O . In the presence of sodium, glaserite forms instead of K_2SO_4 . Complete halite removal from the schoenite concentrate is necessary to produce K_2SO_4 .

Screen analyses of the flotation concentrates obtained under optimum conditions are shown in table 13. Over 32 pct of the schoenite and 29 pct of the sylvite reported to the minus 100-mesh size fractions. Limited testing indicated that the material could be pelletized readily to increase particle size and thus improve market value.

Material Balance and Economic Evaluation

Complete material balances and flow diagrams for the recovery of schoenite and sylvite are shown in appendix figures A-1 through A-6. The material balances are for a plant designed to process 1,000

TABLE 13. - Screen analysis of schoenite and sylvite products, weight percent

Product size, mesh	Schoenite	Sylvite
Plus 65.....	21.1	24.6
Minus 65 plus 100....	46.7	45.8
Minus 100.....	32.2	29.6

ton/d of solar evaporite described in table 10. Economic evaluations of the methods are given in appendix tables A-1 and A-2.

Two options of this process are presented in this report. The first option includes all of the required equipment for the process described. Because the process utilizes brine from an existing plant, the proposed plant is assumed to be an addition to the existing plant. Option 2 does not include equipment to process the sylvite, since technology used in the proposed process to upgrade the sylvite is similar to that currently practiced. Therefore, processing of the sylvite fraction may be assumed to be possible in the existing plant.

The estimated annual operating costs for options 1 and 2 are about \$1.40 and \$1.10 per unit of K_2O , respectively. At current potash prices, this would yield an interest rate of return on investment of less than 3 pct for option 1 and about 9 pct for option 2. To yield a 15-pct return on investment, generally considered the minimum acceptable, the average selling price for potash must be \$2.92 per unit of K_2O for option 1 and \$2.18 per unit of K_2O for option 2.

SUMMARY AND CONCLUSIONS

Laboratory evaporation and flotation techniques were investigated for recovering potash from chloride and sulfate-chloride waste and process brines. Results demonstrated that recovery of potash from both types of brine is technically feasible. Brine evaporation showed that crystallization follows predictable paths and produces similar evaporites for respective sulfate-chloride and chloride brines.

Chloride brines produced evaporites containing 15 to 35 pct sylvite with less than 5 pct carnallite. Potash recoveries in the evaporites ranged from 89 to 99 pct.

Evaporation of sulfate-chloride brines produced three types of evaporites: high-sulfate, low-sulfate, and kainite-bearing. Two high-sulfate evaporites were produced containing 15 and 20 pct leonite or schoenite and 20 and 25 pct sylvite, with 84 and 88 pct K_2O recovery, respectively. Two low-sulfate evaporites were produced containing 10 and 5 pct leonite or schoenite and 5 and 15 pct sylvite, respectively, with 93-pct K_2O recovery in each. The two kainite-bearing evaporites contained 5 and 20 pct kainite and 10 and 20 pct sylvite, with 99 and 93 pct K_2O recovery, respectively.

Flotation of chloride brine evaporites was conducted using amine-Barrett's oil collector. During locked-cycle flotation from the four chloride evaporites, sylvite recovery ranged from 90 to 97 pct, with product grades ranging from 54.3 to 60.3 pct K_2O .

High-sulfate evaporites yielded schoenite and sylvite concentrates using caprylic acid and amine-Barrett's oil emulsion as the respective collectors. Schoenite cleaner concentrate contained 27.8 pct K_2O and was contaminated with sylvite; the overall schoenite recovery was 78 pct. Sylvite concentrate required recleaner flotation and a fresh water spray leach to produce a 59.7-pct K_2O grade concentrate with 80 pct sylvite recovery.

Low-sulfate evaporite, containing 5 pct sulfate mineral, did not produce a suitable schoenite concentrate and was treated by conventional sylvite flotation techniques. Freshwater leaching of a recleaner concentrate recovered 96 pct of the sylvite in a 59.8-pct K_2O grade product.

Kainite, present in evaporites, had to be converted to leonite or schoenite prior to potash beneficiation. Three methods were investigated: (1) 60-min agitation, (2) 40-min agitation-aeration, and (3) 7-day static conversion. The 40-min agitation-aeration method was the most effective in converting all of the kainite to schoenite. The other methods converted the kainite to a mixture of leonite and schoenite. Without conversion of

kainite, only 54 pct of the total potash was recovered as sulfate-type mineral in two stages of rougher flotation. Conversion by the agitation-aeration method followed by froth flotation recovered 95 pct of the schoenite in a two-stage rougher concentrate containing 26.7 pct K_2O .

Based on the data derived from bench-scale investigations of solar evaporation and flotation, large-scale solar evaporation ponds were constructed to produce sufficient sulfate-type evaporite for flotation in a continuous 100-lb/h PRU. Solar evaporation of 10,000 gal of waste brine produced an evaporite containing 24.5 pct schoenite, 20 pct sylvite, and 51.5 pct halite. Over 99 pct of the potassium was recovered in the evaporite.

Operation of a 100-lb/h PRU recovered over 95 pct of the potash in a schoenite concentrate containing 28.0 pct K_2O and in a sylvite concentrate containing 62.3 pct K_2O . The sylvite concentrate is a marketable product, but the schoenite product should be converted to K_2SO_4 . Conversion of the schoenite recovered 58.7 pct of the potassium from the feed to the K_2SO_4 crystallizer in a K_2SO_4 product containing 50.4 pct K_2O .

The processes' economic feasibility was marginal. At current potash prices, an interest rate of return on investment of less than 3 pct would be realized for a new facility and about 9 pct if the process is adapted to fit an existing sylvite processing plant.

REFERENCES

1. Keyes, W. F. Potash. Ch. in Mineral Facts and Problems, Bicentennial Edition. BuMines B 667, 1975, pp. 855-869.
2. Adams, S. S. Potash. Ch. in Industrial Minerals and Rocks. Soc. Min. Eng. AIME, 1975, pp. 963-990.
3. Hicks, W. B. Evaporation of Potash Brines. Ch. in Shorter Contributions to General Geology. McGraw-Hill, 1915, pp. 65-72.
4. Kohler, M. A., T. J. Nordensen, and W. E. Fox. Evaporation From Pans and Lakes. U.S. Weather Bureau (now Natl. Weather Service, NOAA, Dep. Commerce), Res. Paper 38, May 1955, 21 pp.
5. White, E. T., L. L. Bendig, and M. A. Larson. The Effect of Size on the Growth Rate of Potassium Sulfate Crystals. Paper in Analysis and Design of Crystallization Processes. AIChE Symp. Ser., v. 72, No. 153, 1975, p. 47.
6. Choudhari, B. P. Preparation of Schoenite and Sulfate of Potash From Mixed Salts Obtained in Solar Evaporation. J. Appl. Chem. and Biotechnol., v. 21, 1971, pp. 268-269.
7. Huiatt, J. L., R. B. Tippin, and G. M. Potter. Potassium Salt Flotation From Great Salt Lake Evaporites. Trans.-Soc. Min. Eng. AIME, v. 258, 1975, pp. 303-311.
8. Marullo, G., and G. Perri. Process for Concentrating Kainite by Means of Flotation. U. S. Pat. 2,766,885, Oct. 16, 1956.
9. Oka, S., and M. Kadata. Preparation of Potassium Chloride From Carnallite. J. Chem. Soc. Jpn., Ind. Chem. Sect., v. 56, 1953, pp. 337-339.
10. National Oceanic and Atmospheric Administration (Dep. Commerce). Climatological Data--New Mexico. NOAA, Environ. Data and Inf. Serv., Ashville, NC, v. 75-83, 1971-1979.

APPENDIX.--ECONOMIC EVALUATION

By Deborah A. Kramer¹

CAPITAL COSTS

The capital cost estimate is of the general type called a study estimate by Weaver and Bauman.² This type of estimate, prepared from a flowsheet (figs. A-1 through A-6) and a minimum of equipment data, can be expected to be within 30 pct of the actual plant cost.

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²Weaver, J. B., and H. C. Bauman. Cost and Profitability Estimation. Sec. 25 in Chemical Engineers' Handbook, ed. by R. H. Perry and C. H. Chilton. McGraw-Hill, 5th ed., 1973, p. 46.

The estimated capital costs on a second quarter 1982 basis (Marshall and Swift (M and S) index of 745.9) for the two options are shown in table A-1.

A tailings pond has not been included in the capital cost of the proposed plant. It is assumed that the existing plant has a waste pond.

The proposed plant is designed to operate 3 shifts per day, 7 d/wk, 195 d/yr, except some of the unloading facilities, which operate 1 shift per day, 7 d/wk, and the evaporite harvesting, which operates 1 shift per day, 5 d/wk. Solar evaporite is prepared during the warmer

TABLE A-1. - Estimated capital cost¹

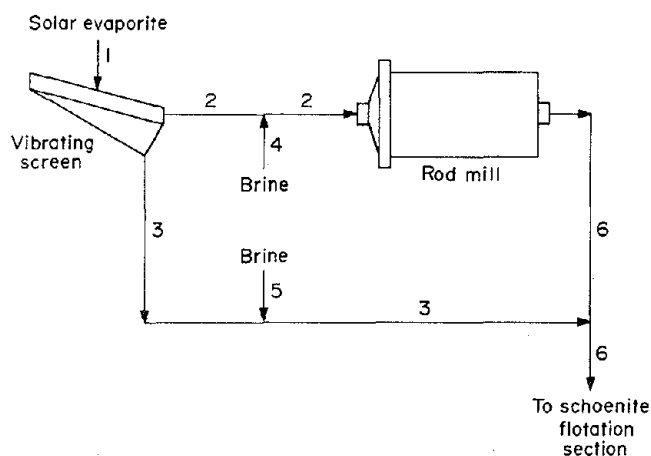
	Option 1 ²	Option 2 ³
Fixed capital:		
Solar evaporation section.....	\$3,494,200	\$3,494,200
Evaporite preparation section.....	2,730,600	2,730,600
Schoenite flotation section.....	294,700	294,700
Sylvite flotation section.....	367,300	0
Schoenite debrining and drying section.....	2,351,500	2,351,500
Sylvite debrining and drying section.....	1,892,600	0
Tailings debrining section.....	1,775,700	0
Steamplant.....	90,200	90,200
Subtotal.....	12,996,800	8,961,200
Plant facilities.....	129,900	89,600
Plant utilities.....	290,200	109,300
Basic plant cost.....	13,316,800	9,160,100
Escalation costs during construction.....	328,900	226,200
Total plant cost.....	13,645,700	9,386,300
Interest during construction period.....	859,200	591,200
Fixed capital cost.....	14,504,900	9,977,500
Working capital cost.....	1,749,000	1,392,800
Capitalized startup costs.....	145,000	99,700
Subtotal.....	1,894,000	1,492,500
Total capital cost.....	16,398,900	11,470,000

¹Basis: M and S equipment cost index = 745.9.

²Combined schoenite and sylvite flotation.

³Schoenite flotation only.

half of the year in 200 acres of ponds, and the processing plant is in operation the remainder of the year.

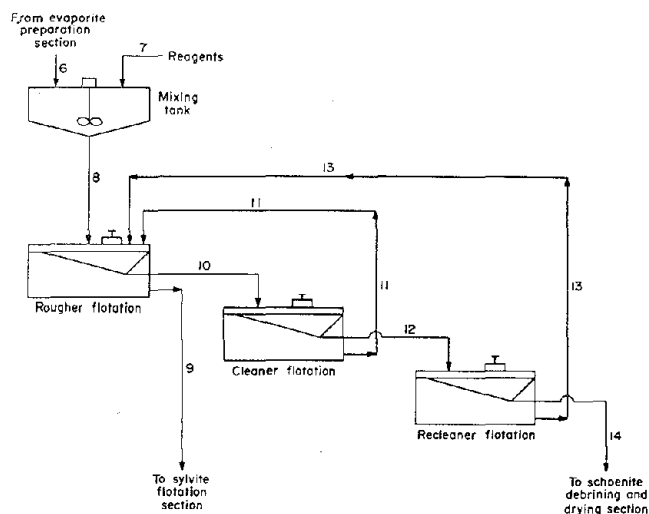


STREAM	1	2	3	4	5	6
SOLIDS, TON/D.....	1,000	600	400	0	0	1,000
BRINE, TON/D.....	0	0	0	600	2,246	2,846
TOTAL	1,000	600	400	600	2,246	3,846

FIGURE A-1. - Evaporite preparation section.

Equipment costs used in this estimate are based on informal cost quotations from equipment manufacturers and on capacity-cost data. In developing the plant capital costs, corrosion-resistant materials of construction are used where appropriate. The tanks and flotation cells are constructed of mild steel, but the rod mill is rubber lined to withstand the corrosive properties of the chloride brine.

Working capital is defined as the funds in addition to fixed capital, land investment, and startup costs that must be provided to operate the plant. Working capital, shown in table A-1, is estimated from the following items: (1) raw material and supplies inventory (cost of raw material and operating supplies for 30 days), (2) product and in-process inventory (total operating cost for 120 days), (3) accounts receivable (total operating cost for 30 days), and (4) available cash (direct expenses for 30 days).

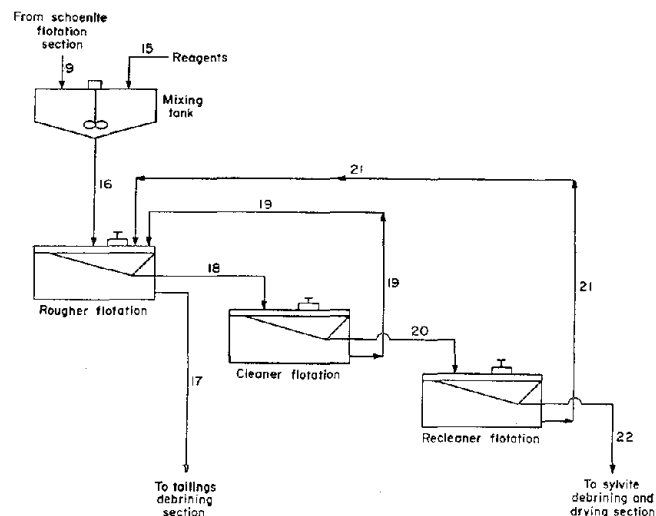


STREAM	6	7	8	9	10	11	12	13	14
SOLIDS, TON/D:									
POTASSIUM	150	0	150	87	70	3	67	4	63
SODIUM	186	0	186	164	37	8	29	7	22
OTHER ¹	664	0	664	478	200	4	196	10	186
BRINE, TON/D:									
K ⁺	120	0	120	95	50	11	39	15	24
Na ⁺	121	0	131	104	58	13	45	18	27
OTHER ²	2,595	0	2,595	2,070	1,115	252	863	338	525
TOTAL	3,846	0	3,846	2,699	1,530	291	1,239	392	347
REAGENT, LB/D:									
CAPRYLIC ACID..	0	200	0	0	0	0	0	0	0

¹CALCIUM, MAGNESIUM, SULFATE, CHLORIDE.

²INCLUDES WATER, CHLORIDE ION, MAGNESIUM, SULFATE.

FIGURE A-2. - Schoenite flotation section.

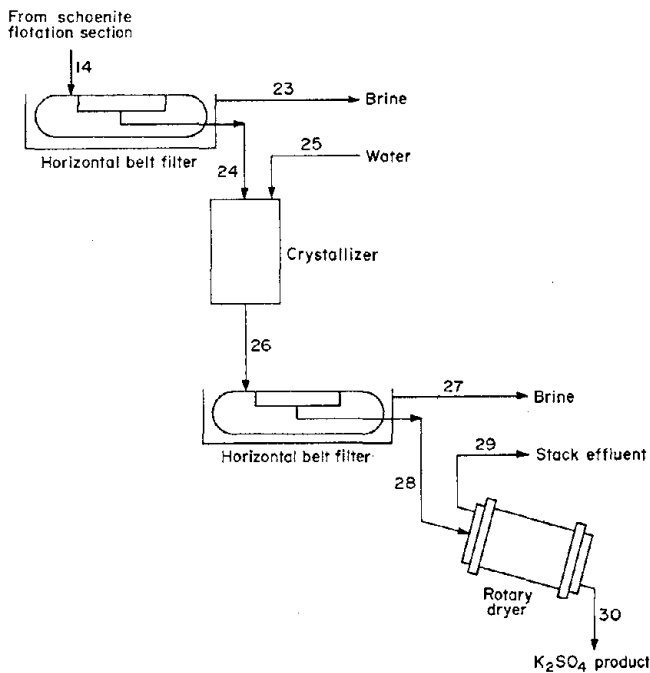


STREAM	9	15	16	17	18	19	20	21	22
SOLIDS, TON/D:									
POTASSIUM	87	0	87	6	90	4	86	5	81
SODIUM	164	0	164	157	21	3	18	11	7
OTHER ¹	478	0	478	395	105	10	95	12	83
BRINE, TON/D:									
K ⁺	96	0	96	63	90	3	36	3	33
Na ⁺	104	0	104	68	42	3	39	3	36
OTHER ²	2,070	0	2,070	1,360	783	9	774	64	710
TOTAL	2,999	0	2,999	2,048	1,080	32	1,048	98	950
REAGENT, LB/D:									
ANLINE-BARRETT'S OIL	0	200	0	0	0	0	0	0	0

¹CALCIUM, MAGNESIUM, SULFATE, CHLORIDE.

²INCLUDES WATER, CHLORIDE ION, MAGNESIUM, SULFATE.

FIGURE A-3. - Sylvite flotation section.



STREAM	14	23	24	25	26	27	28	29	30
SOLIDS, TON/D:									
POTASSIUM	63	0	63	0	37	0	37	1	36
SODIUM	22	0	22	0	4	0	4	0	4
OTHER ¹	186	0	186	0	48	0	48	2	46
BRINE, TON/D:									
K ⁺	24	22	2	0	28	26	2	0	0
Na ⁺	27	25	2	0	20	19	1	0	0
OTHER ²	525	478	47	271	456	427	29	32	0
TOTAL	847	525	322	271	593	472	121	35	86

¹CALCIUM, MAGNESIUM, SULFATE, CHLORIDE.

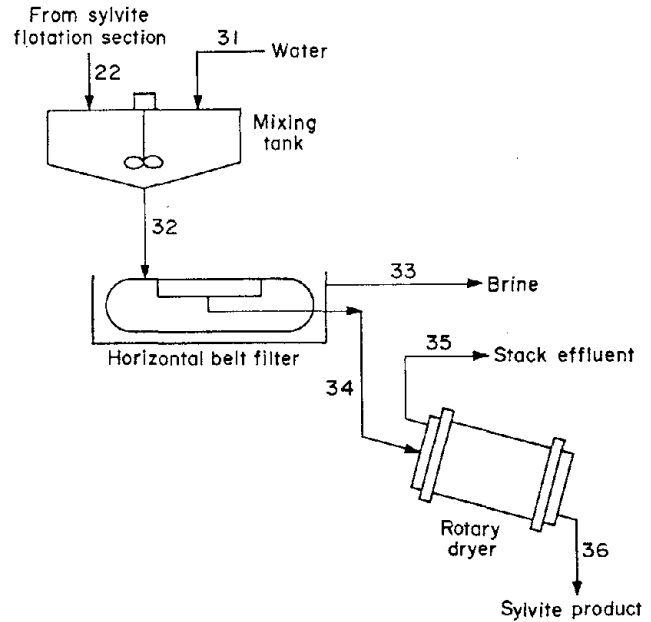
²INCLUDES WATER, CHLORIDE ION, MAGNESIUM, SULFATE.

FIGURE A-4. - Schoenite debrining and drying section.

Startup costs are estimated as 10 pct of the fixed capital costs, of which 1 pct is capitalized and is shown in table A-1. The remaining 9 pct are assumed to be first-year operating costs; however, they are not shown in the operating cost table. These startup costs are used in calculating the required return on investment. Land investment is not included in this estimate.

OPERATING COSTS

The estimated operating costs are based on an average of 195 d/yr of operation over the life of the plant. The operating costs are divided into direct, indirect, and fixed costs.



STREAM	22	31	32	33	34	35	36
SOLIDS, TON/D:							
POTASSIUM	81	0	80	0	80	3	77
SODIUM	7	0	2	0	2	0	2
OTHER ¹	83	0	75	0	75	5	70
BRINE, TON/D:							
K ⁺	33	0	34	32	2	0	0
Na ⁺	36	0	41	38	3	0	0
OTHER ²	710	43	761	707	54	59	0
TOTAL	950	43	993	777	216	67	149

¹CALCIUM, MAGNESIUM, SULFATE, CHLORIDE.

²INCLUDES WATER, CHLORIDE ION, MAGNESIUM, SULFATE.

FIGURE A-5. - Sylvite debrining and drying section.

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. The direct labor cost is estimated on the basis of assigning 4.2 employees for each position that operates 24 h/d, 7 d/wk; 1.4 employees for each position that operates 1 shift per day, 7 d/wk; and 1 employee for each position that operates 8 h/d, 5 d/wk.

Payroll overhead includes vacation, sick leave, social security, and fringe benefits.

Indirect costs include the expenses of control laboratories, accounting, plant protection and safety, plant

administration, marketing, and company overhead. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of taxes (excluding income taxes), insurance, and depreciation. Depreciation is based on a straight-line, 20-yr period.

The estimated annual operating costs for the two processing options are presented in table A-2. No charge has been assessed for the brine in both options. The operating cost for option 2 includes reagents and utilities required to upgrade the sylvite. Even though the sylvite is being processed in the existing

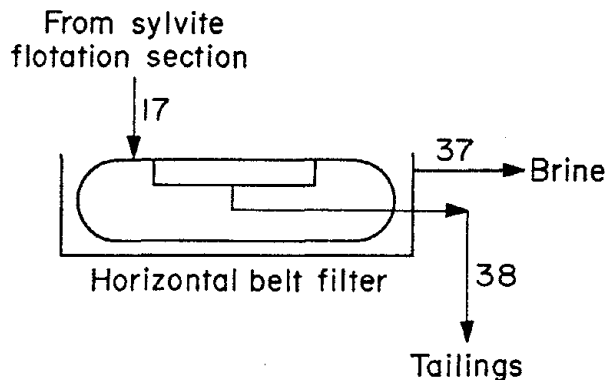
plant, additional reagents and utilities will be required.

TABLE A-2. - Estimated annual operating cost

Option	Annual cost	Cost per unit K_2O
1.....	\$3,767,300	1.423
2.....	2,982,500	1.130

ECONOMIC EVALUATION

Figure A-7 presents a graph of the interest rate of return on investment versus selling price per unit of K_2O for both of the options. The selling price shown is an average selling price per unit of K_2O . (One unit of K_2O is equivalent to 1/100 of a ton, or 20 lb). Two products with different market values are recovered in this process, but both are priced according to the units of K_2O contained. Standard agricultural potassium



STREAM.....	17	37	38
SOLIDS, TON/D:			
POTASSIUM	6	0	6
SODIUM	157	0	157
OTHER ¹	395	0	395
BRINE, TON/D:			
K ⁺	63	59	4
Na ⁺	68	63	5
OTHER ²	1,360	1,271	89
TOTAL	2,049	1,393	656

¹CALCIUM, MAGNESIUM, SULFATE, CHLORIDE.

²INCLUDES WATER, CHLORIDE ION, MAGNESIUM, SULFATE.

FIGURE A-6. - Tailings debrining section.

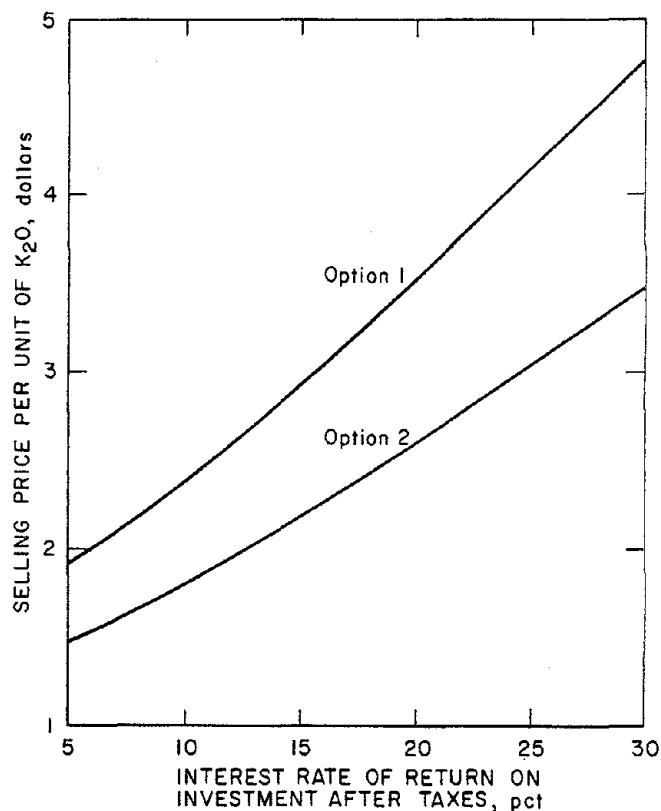


FIGURE A-7. - Interest rate of return on investment.

sulfate must contain a minimum of 50 units of K_2O per ton, and standard muriate of potash contains 62 units per ton. The potassium sulfate produced by the proposed process contains 50 units of K_2O per ton, and the muriate of potash produced contains 62.4 units of K_2O per ton.

In order to determine the average selling price for the combined products, the percent of the total units of K_2O in each product must be determined. A total of 13,600 units of K_2O per day are produced. Potassium sulfate contains 4,300 units, or 31.6 pct of the total, and muriate of potash contains 9,300 units, or 68.4 pct of the total. Multiplying the current selling price of each product by the percent of the total units of K_2O in each and adding these numbers together gives an average selling price. After an average selling price is determined, the rate of return on investment can be found for each option on the graph.

For example, agricultural potassium sulfate is currently selling at \$2.95 per unit and standard muriate of potash is selling at \$1.12 per unit. Thus, the average selling price should be $(1.12)(0.684) + (2.95)(0.316)$ or \$1.70 per unit. From figure A-7, this would yield about a 9-pct return on investment using option 2. Historically, these are very low values, and owing to the cyclic nature of the prices in the potash industry, this return cannot be assumed to be representative of an average rate of return on investment over the life of the plant. To yield a 15-pct return on investment, generally considered the minimum acceptable, the average selling prices for potash produced by options 1 and 2 are \$2.92 and \$2.18 per unit of K_2O , respectively.

Solar evaporation constitutes a major portion of the costs for both options 1

and 2. The other alternative for producing salt crystals from the brine is to use evaporative crystallizers. However, the additional cost of steam required to evaporate the water would prove to be more costly than solar evaporation.

In option 2, it has been assumed that the original plant has surplus capacity to handle the sylvite fraction produced by the proposed process. An alternative would be to reduce mining operations and produce less feed. Plant capacity would be maintained by utilizing the recycled sylvite feed. Lower mining cost could then be used to offset the cost of the solar evaporation ponds.

In evaluating the operating costs of both options, it appears that there are two high-cost areas--utilities and depreciation. Most of the utilities cost is oil used in the dryers. Operating the plant only 6 months per year increases the effect of depreciation on the operating cost. Operating a smaller plant year round to reduce depreciation has been considered but has been rejected as incompatible with the solar evaporation technique. Therefore, it does not appear feasible to reduce costs significantly by modifying the proposed technology.

Presently about 66 pct of the U.S. demand for potash is imported from Canada. The proposed technology can reduce dependence on imported potash and can serve as a means of reducing wastes by recycling. Technical feasibility of this process has been demonstrated, and it could easily be adopted by industry. Comparing the two processing options, option 2 appears to be economically superior. Use of this option depends upon the feasibility of recycling sylvite to an existing plant. This limits its use and requires that the individual plant situation be considered when selecting between options.

