OKLAHOMA GEOLOGICAL SURVEY

Robert H. Dott, Director

Mineral Report No. 14

THE POSSIBILITY OF MAGNESIA FROM OKLAHOMA OIL FIELD BRINES

By A. L. Burwell

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INTRODUCTION

During the more than 40 years of the Oklahoma oil industry, operators have been forced to handle large volumes of salt water or brine, produced along with the oil. Such handling has been a dead expense, and although the brines contain substances of commercial value, all methods for their recovery have been based upon concentration by evaporation and crystallization. Three plants have been built to produce common salt and some byproducts, but two of them succumbed to competition with established salt industries in adjacent states, and the third has never been able to make substantial inroads into this field.

Although sodium chloride (common salt) and calcium chloride make up about 95 percent of the dissolved matter in most Oklahoma brines, substantial quantities of magnesium chloride, and much smaller quantities of other useful materials are commonly present. Whereas the market for Oklahoma-produced sodium chloride is too limited for successful exploitation at this time, the production of magnesium products offers very attractive possibilities, and probably can be made to pay the entire cost of brine disposal and yield a profit.

It is the purpose of this paper to suggest a method whereby magnesium can be extracted and the balance of the brine disposed of in the usual manner. Disposal plants that handle large volumes of brine daily are already installed and in operation throughout the Oklahoma oil fields. Magnesium-extraction equipment could be added with little trouble and its addition would in no way affect the successful operation of the disposal systems.

DISPOSAL OF OKLAHOMA OIL FIELD BRINES

The Disposal of oil field brine has always been a perplexing and expensive problem. Under present practices and regulations, disposal must be in such a manner that the brine will not create a nuisance, destroy vegetation, damage soil, or pollute streams. Subsurface disposal into suitable underground formations has been the most satisfactory method, but to date, disposal of brine has been entirely an expense item, with no financial return of any kind, and any method of salvaging anything of value from the brine, before disposal, should be welcomed by the operators.

Legal control of oil field brine disposal rests with the Oklahoma Planning and Resources Board, and permits for installation of disposal systems are issued by that Board. Table I is a list of permits that have been issued up to July 1, 1942, with location, daily input of brine, and treatment given.

CHEMICAL CHARACTER OF OIL FIELD BRINES

Analyses of oil field brines of Oklahoma show large percentages of sodium chloride and calcium chloride, with varying amounts of magnesium chloride, and much smaller amounts of other elements such as bromine, iodine, strontium, and barium, for which tests are rarely made. Of these ingredients, one which offers commercial possibilities under existing conditions is magnesium chloride. Representative analyses of brines from many of the state's oil fields are given in Table II, through the courtesy of the U. S. Bureau of Mines, Petroleum Experiment Station. An analysis of average sea water is included for comparison.

County	Field	Daily Input Bbls. (42 gal.)	Treatment
Carter	Healdton	35 to 100	Settling - Filtration
Cotton	Walters	40	" "
Cleveland	Moore	3,000	" "
Creek	Slick	150	" --
Creek	Pumpkin Center	500	Aeration - Settling
Creek	"	50	" "
Creek	Harjo	2,000	" "
Creek	Hammer	2,000	" "
Creek	Drumright	500	-- "
Creek	Cushing	200	Aeration - "
Creek	Stroud	100	" "
Creek	-	1,000	-- "
Garfield	Garber	3,000 - 7,000	Aeration - "
Grant	Caldwell, Kansas	800	-- "
Hughes	Adams	200	-- "
Jackson	Tipton	600	Aeration - "
Kay-Osage	Burbank	50	" "
Kay	Hubbard	1,000	" "
Kay	Burbank	600	-- "
Lincoln	Prague	600	-- "
Lincoln	Wilzetta	3,000	Aeration - "
Lincoln	Chandler	500	-- "
Lincoln	Hoyt	1,500	-- "

1/ Data from Oklahoma Planning & Resources Board. (Continued - next page)

Table I (Continued)

County	Field	Daily Input Bbls. (42 gal.)	Treatment
Logan	Lucien	600 to 10,000	Aeration - Settling
Logan	Cresent	2,000	" "
Logan	Lucien	3,000	Settling - Filtration
Noble	Billings	1,000	" "
Noble	–	500	" —
Nowata	Delaware Ext.	12	Closed - Settling
Okfuskee	East Okemah	1,000	Settling —
Okfuskee	Okemah	500	" —
Okfuskee	Olympic	150	Aeration - Settling
Okfuskee	Shelton	100	" "
Oklahoma	N. E. Extension	5,000	" "
Oklahoma	Edmond	4,000	Aeration-Settling-Filtration
Oklahoma	Edmond	865	— " "
Oklahoma	Britton	500	— " —
Okmulgee	Oklahoma Central	300	— " —
Okmulgee	Beggs	1,000	— " —
Okmulgee	Beggs	1,200	— " —
Osage	Burbank	200	Aeration " —
Osage	Burbank	500	" " —
Osage	Burbank	100	" " —
Osage	Burbank	200	" " —
Osage	Burbank	40	— " —
Osage	Burbank	200	— " —
Osage	Woolaroc	35	Closed " —
Osage	Woolaroc	45	" " —

County	Field	Daily Input Bbls. (42 gal.)	Treatment
Osage	Woolaroc	50	Closed " —
Osage	Osage	200	Settling - Filtration
Osage	Osage	550	" "
Osage	Hominy	400	" "
Osage	Hominy	950	" "
Osage	Pershing	50	Aeration - Settling
Osage	Hardy	50	" " —
Osage	Madalene	75	" " —
Pawnee	Cleveland	3,000-4,000	" " —
Pawnee	–	100	— " —
Payne	Stillwater	350	Aeration " —
Payne	Ramsey	800 to 2,000	— " Filtration
Pontotoc	Fitts	2,000	Aeration " "
Pontotoc	Fitts	20,000	" " "
Pottawatomie	Jarvis	500	Evaporation - Dilution
Seminole	Seminole	800	Settling
Seminole	Konawa	500	"
Seminole	Trough	1,500	"
Seminole	Trough	500	"
Seminole	Seminole	2,800	"
Seminole	Wewoka Lake	400	"
Tulsa	–	200	Filtration
Tulsa	Fowler	400	Aeration - Settling
Tulsa	Owasso	1,600	— "
Tulsa	Bird Creek	500	Aeration "
Washington	Ochelata	15	Closed "
Washington	Wichita	500	Aeration "
Woodward	–	500	— "

TABLE II
ANALYSES OF OKLAHOMA OIL FIELD BRINES
(Results in p.p.m.---Na plus K by difference)

Pool	Stratum	Sp.Gr.	Total solids	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)
					CARTER COUNTY					
Fox	Bottom water2/	--	118,230	280	6,520	2,785	34,860	---	49	73,736
Graham	Kirk	--	123,238	nil	6,388	882	39,700	265	1,303	74,600
do.	Graham	--	63,755	112	3,288	1,052	19,750	122	82	39,349
Hewitt	Oil	--	54,416	70	3,504	1,140	15,750	122	nil	33,830
					CREEK COUNTY					
North Cushing										
	Layton	--	116,764	962	8,100	1,754	32,500	---	---	73,408
	Skinner	--	190,166	2,592	12,069	566	55,700	---	---	119,239
	Bartlesville	1.134	195,340	349	12,221	2,562	59,020	24	---	120,564
	Tucker	--	190,807	310	nil	2,649	70,313	73	229	117,233
Slick										
	Dutcher	--	177,200	1,056	9,080	163	66,123	---	90	100,680
	Glenn	--	83,882	962	7,007	831	23,678	---	nil	51,403
					GRADY COUNTY					
Chickasha										
	Nichols, T5N.R8W	--	98,200	---	3,600	3,120	37,154	---	526	56,800
	Nichols, T4N.R8W	--	136,520	---	7,600	5,320	40,325	---	625	81,650

Pool	Stratum	Sp.Gr.	Total solids	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)
					KAY-NOBLE COUNTIES					
Tonkawa										
	Lower Hoover	--	246,818	---	2,770	3,575	88,285	--	274	151,300
	Tonkawa	--	192,176	---	9,662	6,635	54,827	--	93	120,935
					LINCOLN COUNTY					
Davenport										
	Layton	1.125	179,699	---	8,655	2,031	58,090	37	251	110,655
	Prue	1.133	194,637	---	9,899	2,038	62,599	104	142	119,855
	Hunton	1.109	160,427	---	8,014	1,570	54,170	43	888	95,742
					OKFUSKEE COUNTY					
Deaner										
	Deaner	--	160,797	244	9,987	1,787	51,010	----	345	97,400
	Kingwood	--	156,460	441	8,139	1,968	51,600	----	397	93,100
					OKFUSKEE-SEMINOLE COUNTIES					
Cromwell										
	2170 ft.	--	288,353	2,360	20,560	3,355	83,011	----	207	178,490
	1060 ft.	--	85,896	---	4,875	3,110	23,524	73	68	53,899
					OKLAHOMA COUNTY					
Edmond Disposal		1.160	256,800	80	13,504	2,202	72,557	17	324	141,700 516 Br.
Moore (Brine-Disposal System)										
	Point 1	1.150	227,778	41	13,263	2,254	71,566	92	499	140,063

2/ Fox Field, depth 2,280 - 2,334 feet.

(Continued - next page)

Table II (Continued)

Pool	Stratum	Sp.Gr.	Total solids	(Fe)	(Ca)	(Mg)	(Na)	(HCO_3)	(SO_4)	(Cl)
OKLAHOMA COUNTY										
Oklahoma City										
	Tonkawa	1.140	178,520	--	9,820	2,200	56,356	25	9	110,110
	Layton	1.150	189,596	--	12,230	1,846	58,404	6	tr	117,110
	Wilcox	1.15	191,314	--	11,720	2,696	58,287	32	327	118,251
	Lower Simpson	1.165	252,771	--	15,066	2,909	78,494	49	233	156,020
	Arbuckle	1.153	194,324	--	11,590	2,090	60,553	47	244	119,300
PONTOTOC COUNTY										
Fitts (Magnolia-Fitts Brine-Disposal System)										
	Point #1	1.100	141,032	14	7,112	1,979	44,613	67	372	86,875
	Point #2	1.100	143,994	0.2	7,152	1,990	45,723	85	396	88,648
	(Fitts Pool Cooperative System)									
	Point #11	1.097	137,292	26	5,660	1,580	45,497	71	208	84,350
	Point #12	1.113	159,914	11	8,840	2,120	49,917	88	588	98,350
	Point #14	1.111	156,609	7	8,680	2,060	48,894	71	547	96,350
Fitts										
	McAlester	1.040	57,708	11	1,703	846	19,506	79	104	33,459
	Gilcrease	1.075	104,255	25	3,987	2,363	32,970	165	32	64,713
	Cromwell	1.085	119,319	59	4,187	2,396	38,529	146	325	73,577
	Hunton	1.097	141,582	25	5,710	1,507	47,071	177	217	86,875
	Simpson, upper	1.109	161,408	21	8,675	2,151	50,628	128	520	99,285
	Simpson, upper	1.112	167,264	14	9,076	2,254	52,335	61	693	102,831
	Simpson, upper	1.102	150,294	18	7,413	2,049	47,772	104	745	92,193

	Wilcox	1.115	170,189	15	9,937	2,105	52,775	79	674	104,604
	Oil Creek	1.118	175,822	0	10,759	2,505	53,469	159	780	108,150
POTTAWATOMIE COUNTY										
Maud										
	Wilcox	--	168,613	--	8,984	2,198	53,130	47	254	104,000
	Wilcox	--	159,227	--	8,596	1,932	50,276	43	280	98,100
St. Louis										
	Simpson	--	148,250	--	7,950	2,080	46,421	49	350	91,400
	Simpson	1.113	150,194	--	9,416	2,389	45,122	49	67	93,151
	Wilcox	1.122	177,913	--	9,336	2,258	56,317	49	31	109,922
	Wilcox	1.123	178,056	--	10,979	2,446	54,299	12	43	110,277
POTTAWATOMIE-SEMINOLE COUNTIES										
Carr City										
	Wilcox	--	158,789	--	8,280	1,958	50,391	76	284	97,800
	Wilcox	--	150,439	--	7,920	1,804	47,762	61	192	92,700
Earlsboro										
	Calvin	--	161,488	--	11,302	2,214	47,243	12	57	100,160
	Misener	--	135,829	--	7,600	1,358	43,424	49	298	84,100
	Hunton	--	166,594	--	11,410	1,768	50,370	53	293	102,700
	Simpson	--	158,017	--	7,650	1,880	50,883	--	304	97,300
	Wilcox	--	166,850	--	8,735	1,878	53,193	37	173	102,834
	Wilcox	--	165,104	--	8,615	1,987	51,341	55	272	102,834
SEMINOLE COUNTY										
Bowlegs										
	Hunton	1.002	--	--	--	--	--	--	901	--

Table II (Continued)

Pool	Stratum	Sp.Gr.	Total solids	(Fe)	(Ca)	(Mg)	(Na)	(HCO_3)	(SO_4)	(Cl)
(Seminole County - Continued)										
	Wilcox	1.112	164,429	--	9,617	1,891	52,333	73	515	100,000
Little River										
	Cromwell	--	139,190	--	7,760	1,988	43,206	146	90	86,000
	Wilcox	--	172,525	--	10,620	1,936	53,268	46	455	106,200
	Wilcox	--	143,968	--	7,380	1,720	45,922	---	346	88,600
Mission										
	Hunton	--	172,930	--	9,730	1,604	54,931	51	464	106,150
	Wilcox	--	170,252	--	10,040	1,880	53,121	37	374	104,800
	Wilcox	--	157,433	--	8,800	1,820	49,505	28	280	97,000
Searight										
	Calvin	--	105,068	--	7,180	1,672	30,932	--	54	65,230
	Misener	--	152,591	--	7,190	1,482	49,875	--	244	93,800
	Hunton	--	154,858	--	7,482	1,494	50,350	67	1,055	94,410
	Wilcox	--	148,887	--	7,740	1,660	47,573	16	298	91,600
Seminole City										
	Hunton	1.110	160,401	--	8,976	1,623	50,720	31	827	98,224
	Simpson	1.113	157,071	--	8,414	1,743	49,867	55	542	96,450
	Wilcox	1.106	153,337	--	8,615	1,498	48,537	110	608	93,969
	Wilcox	1.106	151,708	--	8,014	1,636	48,374	18	406	93,260
Sea Water (after Dittmar)3/		--	34,400	--	409	1,279	10,903	73	2,649	19,085

3/ Cited by Emmons et al, "Geology", McGraw Hill, New York, 1939, 2nd edition.
Source of information on brines: See "References, Table II", next page.

References, Table II

"Petroleum Engineering in The Fox and Graham Oil and Gas Fields, Carter County", U. S. Bur. of Mines, in cooperation with Office of Indian Affairs, State of Oklahoma, and Ardmore Chamber of Commerce, 1924.

"Water Problems in the North Part of the Cushing Oil Field, Creek County, Okla.", U.S. Bur. of Mines, in cooperation with the State of Oklahoma, 1927.

"Petroleum Engineering in the Slick Oil Field, Creek County, Oklahoma", U. S. Bur. of Mines in cooperation with the State of Oklahoma and Bartlesville Chamber of Commerce, 1922.

"Engineering Report on the Chickasha Gas Field, Grady County, Okla.", U.S. Bur. of Mines, in cooperation with the State of Oklahoma and Bartlesville Chamber of Commerce, 1923. "Supplemental Engineering Report on the Chickasha Gas Field", 1926.

"Preliminary Report on Petroleum Engineering in the Tonkawa Oil Field, Kay and Noble Counties, Okla.", U.S. Bur. of Mines, in cooperation with the State of Oklahoma, 1923.

"Engineering Report on the Davenport Field, Lincoln County, Okla.", U.S. Bur. of Mines, in cooperation with the State of Oklahoma and Bartlesville Chamber of Commerce, 1926.

"Petroleum Engineering in the Deaner Oil Field, Okfuskee County, Okla.", U. S. Bur. of Mines, in cooperation with the State of Oklahoma and Bartlesville Chamber of Commerce, 1921.

"Petroleum Engineering in the Cromwell Oil Field, Seminole and Okfuskee Counties, Okla.", U.S. Bur. of Mines, in cooperation with Office of Indian Affairs and State of Oklahoma, 1924.

"Typical Oil-Field Brine Conditioning Systems: Preparing Brine for Subsurface Injection", U.S. Bur. of Mines, Rept. Investig. 3434, 1939.

"Engineering Report on the Oklahoma City Oil Field, Oklahoma", U. S. Bur. of Mines, Rept. Investig. 3330, 1937.

"Subsurface Disposal of Oil-Field Brines in Oklahoma", U. S. Bur. of Mines, Rept. Investig. 3603, 1942.

"Engineering Study of the Seminole Area, Seminole and Pottawatomie Counties, Okla.", U. S. Bur. of Mines, Rept. Investig. 2997, 1930.

RECOVERY OF MAGNESIUM FROM BRINE

A method for the recovery of magnesium from the brine in the form of magnesium hydroxide seems to offer the best possibilities. The process is based upon the reaction between magnesium chloride and calcium hydroxide whereby insoluble magnesium hydroxide is precipitated and calcium hydroxide is converted to soluble calcium chloride. Inasmuch as the exchange is in molecular proportions there is no disturbance of the "stability" of the brine for subsequent underground disposal, unless excess of calcium hydroxide is introduced. The process is now in commercial operation at Freeport, Texas, extracting the magnesium from sea-water.

Other than the brine, the raw material required is calcined limestone (quicklime, calcium oxide) or calcined dolomite (calcium oxide and magnesium oxide). The advantage derived from the use of dolomite rather than limestone lies in the fact that magnesium recovery is from both the brine and the dolomite, and is therefore proportionally greater. The precipitation and sedimentation of magnesium hydroxide and its removal from the brine presents a number of technical problems that vary with individual brines, with particular limes and dolomites, and even with the method of "burning". Therefore, it is not possible to offer any specific suggestions as to standard size or kind of equipment for a plant. Each prospective plant will need be designed following tests on the brine and the stone.

The accompanying sketch of a representative flow

sheet illustrates the basic idea. If iron is present, the brine is first aerated, whereby the iron separates and is then removed along with any other suspended matter by sedimentation or filtration. In the process illustrated by the flow sheet, "milk of dolomite", made by calcination and slaking, is fed into the clarified brine in a flocculator. Reaction takes place between the calcium hydroxide from the dolomite and the magnesium chloride from the brine, whereby calcium chloride goes into solution and magnesium hydroxide separates as an insoluble floc. As a result of the calcium hydroxide of the calcined and slaked dolomite having gone into solution, an insoluble residue of magnesium hydroxide from the dolomite is left. The brine now contains in suspension the magnesium hydroxide from both the dolomite and the brine, and is transferred to a "thickener" which concentrates the suspended magnesium hydroxide in a smaller volume of brine, the less brine the better.

There is the choice as to whether further processing for the removal of chlorides and other solubles should be carried out and some specific magnesium product prepared ("A" on flow sheet), or whether this impure magnesium hydroxide containing an appreciable quantity of "solubles" from the brine should be dried and shipped as such ("B" on flow sheet). In either event further dewatering is brought about in mechanical filters. The filter cakes may be dried, disintergrated or otherwise prepared for the trade as magnesium hydroxide, or calcined under controlled conditions and offered as "caustic calcined"magnesia or as "dead-burned" magnesia.

The reactions involved and theoretical discussion of yields follows:

TABLE III

REACTING EQUIVALENTS, BY WEIGHT, OF COMPOUNDS

Magnesium metal, Mg	1.00
Magnesium chloride, $MgCl_2$	3.92
Magnesium hydroxide, $Mg(OH)_2$	2.40
Magnesium oxide (magnesia), MgO	1.66

Calcium oxide (quicklime), CaO	2.30
Calcium carbonate (limestone), $CaCO_3$	4.12
Calcium-Magnesium carbonate(dolomite)$CaCO_3.MgCO_3$.	7.58

(1) $CaCO_3MgCO_3 + \text{heat} \longrightarrow CaO + MgO + 2CO_2$

(2) $CaO + MgO + 2H_2O \longrightarrow Ca(OH)_2 + Mg(OH)_2$

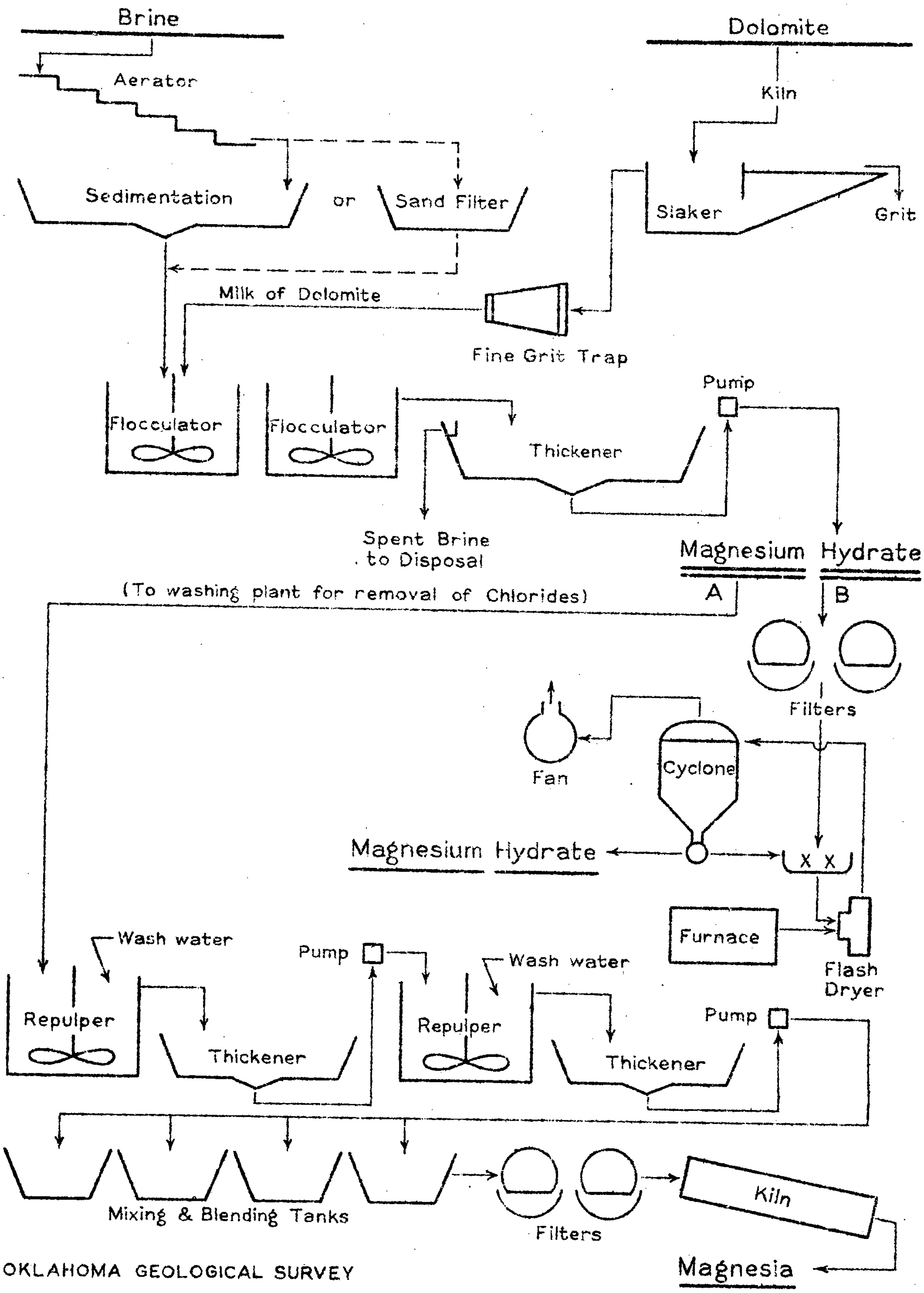
(3) $Ca(OH)_2 + MgCl_2 \longrightarrow CaCl_2 + Mg(OH)_2$

(4) $Ca(OH)_2 + Mg(OH)_2 + MgCl_2 \longrightarrow CaCl_2 + 2Mg(OH)_2$

Reaction (1) represents the calcination of dolomite.
Reaction (2) represents the preparation of "milk of dolomite" by hydration.
Reaction (3) represents the action of the calcium hydroxide in the "milk of dolomite" on the magnesium chloride in the brine.
Reaction (4) Represents the total exchange when "milk of dolomite" is added to a brine containing magnesium chloride. The magnesium hydroxide is the sum total produced from the brine and the dolomite.

The average Oklahoma oil field brine contains approximately 2,000 p.p.m. magnesium in the form of magnesium chloride, and has a specific gravity of about 1.1 and weighs 9.171 pounds to the gallon as compared to distilled water with a specific gravity of 1.0 and weight of 8.337 pounds to the gallon. The oil field barrel has 42 gallons capacity. Hence, one million pounds of brine is 2,596 barrels and contains 6,840 pounds of magnesium chloride (2,000 pounds of magnesium). Further computation shows that 1,000 barrels of this average brine will require 3,175 pounds of pure limestone (1,770 pounds of quicklime) to yield 1,850 pounds of magnesium hydroxide (1,280 pounds of magnesium oxide). In like manner, 1,000 barrels of brine will require 5,840 pounds of dolomite (3,051 pounds of calcined dolomite) and will yield 3,700 pounds of magnesium hydroxide (2,560 pounds of magnesium oxide) half from the brine and half from the dolomite.

A Representative Flow Sheet
Magnesia from Oil Field Brines



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These figures are based upon theortically pure limestone and dolomite and theoretically complete reactions and recovery. In commercial operations the purity of the finished product will naturally depend upon the composition of the limestone or dolomite used and upon the technical skill employed and care exercised. The percentage recovery will be governed, in addition to these factors, by limitations imposed by the necessity of leaving the residual brine in a condition suitable for subsurface disposal or of further conditioning to render it so.

PREPARATION FOR THE MARKET

If the magnesium hydroxide is to be converted to other magnesium products at the parent plant it may be advisable for certain purposes to treat the water slurry directly rather than to filter and calcine. Where this is not the case and depending upon the ultimate use, the product of the mechanical filter (see flow sheet) called "filter cake" may be used as it is or subjected to fresh water washing while in the filter to remove soluble salts retained from the brine. The washed or unwashed filter cake may be calcined to produce magnesium oxide of required purity, or may be subjected to several methods of treatment in order to produce a variety of magnesium products that are of commercial importance. The following outline summarizes the various methods of treatment and products from magnesium hydroxide and their uses.

Magnesium oxide. Calcination or dehydration of magnesium hydroxide converts it into the oxide. If calcination is carried out at temperatures between 700 and 1000°C.,the product is classified as "caustic magnesia" and suitable for magnesia cements and other chemical purposes. By raising the temperature to 1450 to 1500° C. in the presence of sufficient iron, or to 1600 to 1700° C. in the absence of impurities, the product is classified as "dead-burned" magnesia, and is suitable for refractory purposes. If the temperature is still further raised to above 1700°C. in an electric furnace, a hard flinty product is obtained known as "artificial periclase", which shows no additional shrinkage on further heating, and finds use in electric insulators and special crucibles and crucible linings. Magnesium oxide is used in the manufacture of ceramics, magnesia cements, Sorel cement, refractories, crucibles, furnace linings, open-hearth steel furnaces, pipe coverings, paper, heat insulating compounds, stucco, fireproofing compounds, face powder, toilet preparations, mineral waters, paints, varnishes, fertilizers; in copper smelting; dry cleaning fabrics; as rubber filler, fat splitting agent, as polishing medium; and in medicine.

Magnesium chloride. Magnesium hydroxide or oxide dissolves in hydrochloric acid to form the chloride. The hydroxide slurry from the thickener or the cake from filters, or "caustic calcined" magnesia, may be used. Magnesium chloride is offered to the trade (1) as the crystalline salt $MgCl_2 6H_2O$; (2) as a flake which is a partially dehydrated material; (3) as anhydrous material. Magnesium chloride is used in the manufacture of ceramics, magnesia cements, magnesium salts, magnesium metal, hydrochloric acid, flooring and fire extinguishing compounds, stucco, paper, thread lubricant, textile size; in dyeing, carbonizing wool, fireproofing wood, treating mine timbers and railroad ties; and in medicine.

Magnesium sulfate. Magnesium hydroxide or oxide dissolves in sulfuric acid to form the sulfate. The hydroxide slurry from the thickener or cake from the filters, or "caustic calcined" magnesia may be used. Magnesium sulfate is offered to the trade (1) as a low-grade, impure product designated as "fertilizer" grade; (2) as the crystalline product, Epsom's Salts, $MgSO_4 . 7H_2O$, and in both technical and USP grades. Magnesium sulfate is used in the manufacture of motion picture snow, dry colors, printing ink, cosmetic lotions, frosted paper, mineral water, ceramics, matches, explosive compositions; as a mordant assist in dyeing and printing textiles; in fertilizers; in fireproofing and waterproofing textiles; in sizing paper; in tanning; and in medicine.

Magnesium carbonate. When solutions of magnesium chloride or sulfate are treated with sodium bi-carbonate, a precipitate of normal magnesium carbonate is

formed and sodium chloride or sulfate remains in solution. However, if sodium carbonate is used in place of the bi-carbonate, then a basic magnesium carbonate is precipitated. Furthermore, when carbonic acid gas (carbon dioxide) is passed into a slurry of magnesium hydroxide the magnesium will pass into solution in the form of the bi-carbonate. Heat will decompose this solution and normal magnesium carbonate will precipitate. Both normal and basic magnesium carbonate are commercial products available in technical and USP grades, and are used in manufacturing other magnesium salts, fire-resistant paints, dry colors, printing ink, ceramics, glass, cosmetics, tooth-paste, face-powder, varnish, refractories, polishing and fire-proofing compounds, boiler scale compounds, free-running table salt, acid neutralizing fertilizers; in heat insulating electric furnace construction; in dairy products; as filler in paint, pigment, paper, linoleum, and oil cloth; pigment in rubber compounding; as general filter medium; and in medicine.

Magnesium metal. Electrolysis of fused anhydrous magnesium chloride produces metallic magnesium and gaseous chlorine. The metal is also produced from dolomite by reduction with ferrosilicon, and from the oxide or carbonate by electrothermic reduction with carbon under very specific condition, details of which can not be gone into in this paper. Magnesium metal is largely used as an alloy with aluminum or other metals, but is also used in the manufacture of flash-light powders, ribbon flash sheets, pyrotechnics, incendiary bombs, military flares, hydrogen, ceramics, organic chemicals, optical mirrors, scientific instruments, automobiles and aeroplanes; in electric batteries; in refining nickel alloys; deoxidizing brass and bronze.

Magnesium silicate. A synthetic product similar in composition to natural talcum may be made by the reaction between soluble salts of magnesium such as the chloride or sulfate and sodium silicate whereby magnesium silicate precipitates and sodium chloride or sulfate remains in solution. Magnesium silicate is used in ceramics; refractories; in paints, lacquers, varnishes; in rubber compounding; as an oil bleaching agent.

Magnesium silicofluoride. This is a water-soluble product resulting from the action of hydrosilicofluoric acid on magnesium hydroxide or oxide. It is offered to the trade as a white crystalline powder or as a solution of 30 percent strength, which are used in ceramics; as insecticides; in hardening and water-proofing concrete.

Magnesia brick. Brick supplied under this name are essentially magnesium oxide, but the composition may vary from as much as 8 percent iron oxide (Fe_2O_3) to nearly iron free. Finely ground dead-burned magnesia with a small amount of water is usually molded in a power press, dried, and again burned. The standard 9-inch brick (9 x 4½ x 2½ inches) vary in weight from 9½ to 10 pounds, and are used in kilns, furnaces, and converters, wherever basic refractory brick is indicated.

Magnesium Oxychloride cements. When caustic magnesia is mixed with a solution of magnesium chloride, preferably of 20 to 22° Be' gravity, a plastic cement is formed which is quick-setting to a hard, dense, tough consistancy that can be drilled, planed, and buffed to a durable high gloss finish. Flooring compositions, plaster board, stucco compositions, etc., have been manufactured from magnesia, magnesium chloride, wood fibre, asbestos, coloring matter, and other inert fillers.

SUPPLIES OF LIMESTONE AND DOLOMITE

From a consideration of the method advocated, it is evident that limestone and dolomite of the highest possible quality are desirable if available at reasonable cost, and that the amount and kind of impurities present in the stone may carry on through the process and affect the quality of the finished product. High-calcium limestones and dolomites of almost theoretical composition, occur at several localities in Oklahoma within easy access to transportation. There are three lime kilns operating in Oklahoma at this time. It would appear, therefore, that all essential raw materials are available at minimum cost. Analyses of several Oklahoma limestone and dolomite deposits of suitable grade are given in Table IV.

REPRESENTATIVE ANALYSES OF OKLAHOMA LIMESTONES AND DOLOMITES OF CHEMICAL GRADE

County	Location	Insol.	R_2O_3	CaO	MgO	CO_2	Total	Thickness	Overburden	Formation
Choctaw	17-5S-16E	0.56	0.94	55.38	nil	43.45	100.75	25 ft.	0	Goodland
Johnston	4-2S-8E	0.98	0.57	55.16	nil	43.28	99.99	70 ft.	0	Wapanucka
Ottawa	1-26N-23E	0.38	0.34	55.63	nil	43.65	100.00	10 ft.	15 ft.	Boone
Pontotoc	12-1N-6E	0.87	0.58	54.35	0.60	43.00 / 0.56 moisture	99.96	8 ft.	0 to 5 ft.	Bromide
Sequoyah	13-13N-23E	0.84	0.37	55.66	nil	43.67	100.54	100 ft.	0 to 38 ft.	St. Clair
Blaine	31-15N-11W	1.44	1.46	31.88	19.42	45.66	99.68	2 ft.	0 to 20 ft.	Relay Creek
Comanche	20-2N-12W	0.58	1.04	30.60	20.66	47.17	100.05	40 ft.	---	Strange
Johnston	22-2S-4E	0.53	0.50	30.95	21.43	47.07	100.48	15 ft.	0	Upper Royer
Johnston	26-2S-4E	0.83	0.53	30.64	21.36	46.47	99.83	100 ft.	0	Lower Royer
Kiowa	25-6S-16W	0.72	0.54	30.95	20.70	47.70	100.61	80 ft.	---	Kindblade
Murray	7-2S-2E	0.38	0.76	31.03	20.78	47.34	100.29	27 ft.	---	Royer

COST FACTORS

No attempt is made to estimate costs of plant equipment and installation. The wide variation in size, type, and amount of equipment required because of technical problems of flocculation and sedimentation with different brines, limes and dolomites, makes each installation an individual problem, and no average plant cost can be calculated. Also, plant requirements, and therefore costs, will depend upon the purity specifications demanded in the finished product.

Raw material costs, however, can be stated roughly. Chemical quality quicklime is priced at about $7.00 per ton at the kiln in this territory (Oklahoma, Arkansas, Missouri). So far as is known to the writer, no dolomite is calcined in this territory at the present time, but the cost at the kiln if and when it is available should be about the same as quicklime. The cost of brine where the extraction plant is in connection with existing or proposed brine disposal plant need not be charged against magnesia recovery. If brine is produced specifically as a raw material for this process, then the cost of drilling both the brine well and the disposal well and the producing of the brine (all variable to a wide degree) will need to be calculated and charged against the recovery.

For the operator who wishes to erect his own kiln, either vertical or rotary, and do his own calcining, it may be stated that limestone has a value at the quarry of from $1.00 to $2.00 per ton. Vertical kilns require lump stone and small and fine material from the quarry must be discarded, whereas the rotary kiln, costing much more to install, will handle small and fine stone. There are no commercial quarries producing dolomite in Oklahoma at this time, but cost should be comparable to limestone.

Control in the calcination of dolomite is somewhat more complicated but the temperature required is less

than for limestone, so the cost of calcination should be little if any higher.

Fuel costs will vary smoewhat with the type and quality used, although all types are competitive, and costs calculated to a B.t.u. basis will be comparable. Oklahoma coals have calorific values ranging from 10,000 to over 14,500 B.t.u. per pound. In 1934 the average price per ton of coal in Oklahoma was $2.34 at the mines. Natural gas in Oklahoma will run usually from 900 to 1,350 B.t.u. per cubic foot and will vary in price according to the location, but will probably figure at 10 cents or more per 1,000 cubic feet, except where surplus quantities are available and special concessions made to large industrial users.

Cost data on the following items will have to be ascertained in order to estimate expenditures for plant, materials, and operating costs:

(1) Cost of quicklime or calcined dolomite.
- (A) Cost of quicklime or calcined dolomite, f.o.b. brine treating plant (magnesium recovery plant).
- (B) Cost to manufacture quicklime or calcined dolomite.
  - (a) Cost of construction of kiln at the plant.
  - (b) Amortization of equipment and buildings.
  - (c) Cost of stone, f.o.b. the plant.
  - (d) Cost of fuel and power.
  - (e) Cost of labor.
  - (f) Overhead.

Cost of quicklime or calcined dolomite and the output of the kiln should be calculated on the assumption that the available calcium coming from the slaker will not be over 90 percent of that in the original stone.

(2) Cost of brine treating plant.
- (A) Cost of construction of the brine treating and magnesium recovery plant.
- (B) Amortization of equipment and buildings. Slaker, grit trap, flocculator, thickener, repulper, tanks, filters, kiln, furnace, etc.
- (C) Cost of brine (if produced or purchased for ex-

traction).

(D) Cost of power, water, and fuel. (If installation includes kiln for burning stone, waste heat may be used to dry or calcine the magnesium hydroxide).

(E) Cost of labor.

(F) Overhead.

Output of magnesium hydroxide, or calcined magnesia, should be calculated on the assumption that the brine and dolomite will yield not over 85 percent of their total magnesium content.

Against these costs, the expected income can be based upon the selling price of caustic calcined magnesia, which in 1939, was $30.56 per ton. Additional operations for purification or conversion to other materials will enhance the value probably in proportion to added cost. Production and values of magnesium products are given in Tables V and VI. Included in this list are materials which can be considered as competitive with brine as a source of raw material as well as materials that are directly competitive with finished products obtainable from the brine and dolomite.

CONSUMPTION, VALUE, AND DOMESTIC PRODUCTION OF MAGNESITE AND MAGNESIUM OXIDE
(from Minerals Yearbook, 1940)

	1925-29*	1930-34*	1935	1936	1937	1938	1939
Dead-burned magnesite sold by U. S. producers short tons	47,158	34,935	72,438	89,979	83,204	38,733	86,077
Aver. value per ton	$23.85	$18.33	$18.80	$19.04	$19.24	$18.87	$19.75
Domestic production percent of total	45.33	62.3	74.6	67.9	59.8	60.8	66.0
Caustic calcined magnesite sold by U. S. producers. Short tons.	16,214	6,705	6,049	7,899	10,031	7,400	10,157
Aver. value per ton	$33.20	$30.30	$28.16	$27.68	$31.04	$30.88	$30.56
Domestic production percent of total	60.3	73.7	80.8	78.5	78.2	83.6	82.1

Crude magnesite ($MgCO_3$) Average realized by sales (1939) 198,980 tons @ $14.03 per ton

* Figures for years 1925-29 and 1930-34 are annual averages. (Continued -- next page)

Table V (Continued)

(1939 prices from Eng. & Min. Journal)	per ton
Dead burned magnesite	$22.00 - $25.00
Artificial periclase (94 percent MgO)	$65.00
Artificial periclase (90 percent MgO)	35.00
Caustic calcined magnesite (95 percent MgO) color white	40.00
Caustic calcined magnesite (85 percent MgO) no color standard	37.50
Magnesite brick (9 inch straight)	67.00

OTHER PRODUCTS WHICH MAY BE MADE FROM MAGNESIUM HYDROXIDE OR OXIDE

	Tonnage		Prices 1939	Prices 1942
Magnesium metal, 99.8%	1939	5,000	20 to 30¢ lb.	22½¢ lb.
	1941	17,000		
Expectations	1943	300,000		
Magnesium oxide, powdered		(ton)	$58.00 to $66.00	$58.75
Magnesium oxide, USP light		(lb.)	20 to 25¢	20¢
Magnesium oxide, heavy		(lb.)	25 to 30¢	25¢
Magnesium chloride, flake, 97% $MgCl_2.6H_2O$		(ton)	$39.00 to $42.00	$32.00
Magnesium chloride, anhydrous		(lb.)	----	13¢
Magnesium sulfate, fertilizer grade			(ton) $13.00	----
Magnesium sulfate, technical)	1939	41,000	(ton) 36.00	$36.00
Magnesium sulfate, USP)			(ton) 40.00	40.00
Magnesium carbonate, precipitated, technical	1937	7,300	(lb.) 5½ to 6½¢	6¼¢
Magnesium carbonate, precipitated, USP			(lb.) ----	9¢
Magnesium silicofluoride, technical			(lb.) 10 to 10½¢	20¢

SUMMARY

A method for the extraction of magnesium from oil field brine, which has been approved as technically sound by good authority, has been outlined. The situation as far as raw materials in Oklahoma is concerned is shown to be excellent. An outline of the several products which may be made and something of the present and past market conditions, volume and values, has been given. Factors which must be determined in figuring costs have been set forth.

The consideration at this time of the utilization of Oklahoma brines and dolomite as a source of magnesium was brought about by the desire to cooperate in relieving the shortage of an essential strategic material for war purposes, and the utilization of an abundant material that to date has been only a waste product. Changes in the demand for magnesium hydroxide or oxide as a raw material in the production of magnesium metal will affect and possibly determine the extent to which Oklahoma brines may contribute to the war effort, but we should not lose sight of post-war industrial requirements and the vital need for employment expansion if Oklahoma is to survive industrially. Magnesia is a basic commodity upon which numerous industries are dependent, and to which such industries will normally be attracted by adequate supply and reasonable costs.