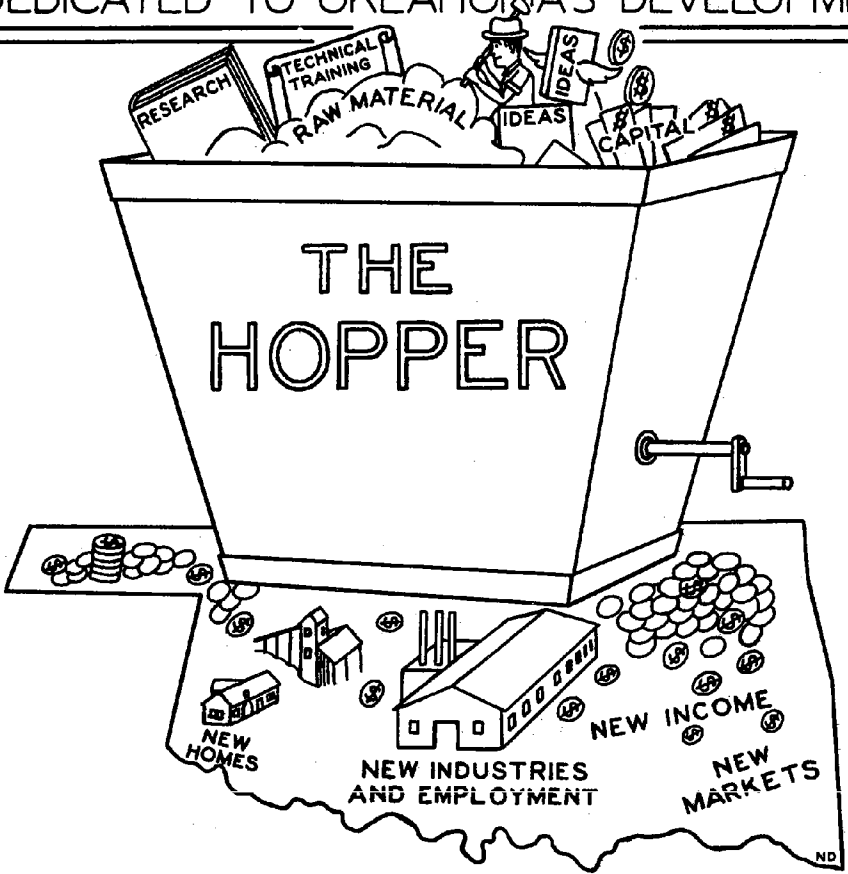


DEDICATED TO OKLAHOMA'S DEVELOPMENT



PUBLISHED IN THE OFFICE OF THE  
OKLAHOMA GEOLOGICAL SURVEY  
NORMAN, OKLA.

Volume 12, No. 3

March, 1952

## Report of Investigation

### Oklahoma Oil-Field Brine

by

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From time to time the question is raised as to what use can be made of oil-field brine. Can the brine be processed by methods that are economically feasible? Can the brine be purified so that it is acceptable raw material for the manufacture of soda ash or for electrolytic production of caustic soda and chlorine? What treatment is necessary in order that the brine may be utilized as a source of crystallized salt? Of what value are the by-products? Is there sufficient brine to justify further research on its possibilities?

Taking the last question first, no estimate has been made nor is it probable that one can be made with any pretense of accuracy. Such an estimate would involve the volume of recoverable brine and a knowledge of kinds and amounts of dissolved solids. It is known that the dissolved solids in Oklahoma oil-field brine range from 54,000 parts per million and lower to as high as 257,000 parts per million, with 150,000 parts per million as the approximate average. It is known, also, that great as has been the volume of petroleum recovered and estimated as recoverable the volume of brine occurring in the same geologic formations must be very many times greater. The tonnage of recoverable dissolved solids is without doubt so tremendous that any conceivable use would have an inexhaustible supply.

An oil-field brine from the Fitts pool is representative of the average for Oklahoma. Analysis gave the following results.

Sp. Gr.	1.113	
Acid insolubles	14	parts per million
Fe <sub>2</sub> O <sub>3</sub>	87	parts per million
Al <sub>2</sub> O <sub>3</sub>	17	parts per million
Ca/Sr	8,675	parts per million
Mg	1,833	parts per million
Na/K	46,084	parts per million
SO <sub>4</sub>	556	parts per million
Cl	91,500	parts per million

The method for purification of such brine will depend upon the use to which the brine or salt produced from the brine will be put. In any event the iron, alumina, suspended matter, and any residual oil should be removed. This can be accomplished by raising the pH of the brine to approximately 8, aeration, and filtration. In treating the brine, analysis of which is given above, 0.38 grams hydrated lime per liter was added, followed by 6 hours exposure to the air, and then filtration through a rapid-sand filter. The filter operated at a rate equivalent to 90 gallons per square foot surface per hour.

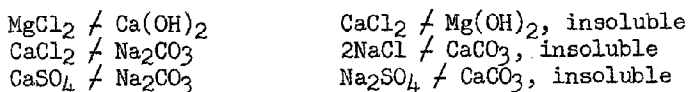
The composition of the clarified brine was calculated from its analysis:

Sp. Gr.	1.107	
CaSO <sub>4</sub>	0.46	grams per liter
SrSO <sub>4</sub>	0.56	grams per liter
CaCl <sub>2</sub>	26.29	grams per liter
MgCl <sub>2</sub>	7.80	grams per liter
KCl	2.56	grams per liter
NaCl	128.39	grams per liter

If the brine is to be evaporated to produce crystallized salt, this simple clarification is all that is usually necessary. If, however, the brine is to be utilized directly for the electrolytic production of caustic soda and chlorine or for the production of soda ash by the Solvay process, it is advisable to remove as much as possible of the dis-

solved matter other than alkali chlorides, namely sodium and potassium chlorides. Sulfates may be removed by treatment with barium carbonate, or the sulfate ion removed and replaced by chloride ion by addition of barium chloride in an amount molecularly equivalent to the sulfates. If such treatment is to be used it should preferably be done prior to or as a part of the clarification.

For the removal of calcium and magnesium compounds the standard procedure makes use of the following reactions with hydrated lime and soda ash:



Accordingly "soda ash is fed continuously into a high-speed dissolving tank through which flows part of the brine to be treated. This solution is then mixed with the balance of the brine and is then passed through a series of slow-speed reaction tanks for the purpose of completing the reaction (which takes an appreciable time), and for the purpose of improving the settling properties of the precipitated calcium carbonate. Milk of lime is generally added to one of these reaction tanks if magnesium is to be precipitated." 1/

In the ammonia-soda (Solvay Process) plants it is common practice to maintain an excess of about 0.8 grams  $Na_2CO_3$  per liter and an excess of somewhat more than 0.15 grams lime per liter.

Purification of Oklahoma oil-field brine by chemical treatment is not economically feasible, in most cases. The cost of soda ash, lime, and barium compounds at prevailing market prices would be more than \$6.00 for every ton of sodium chloride contained in the brine. This is prohibitive, of course. The logical procedure, therefore, is to eliminate as much as possible of the impurities by

Table I.

. Salt (a) . Salt (b) . Rock salt<sup>2/</sup> . Sea-salt<sup>2/</sup> . Bittern,  
 Solar evap. Pan evapor. from salt (b)  
 Clar. brine. Clar.&sulfate  
 free brine.

	Percent	Percent	Percent	Percent	gms. per liter.
H <sub>2</sub> O, free & comb.	2.37	1.02	0.34	7.66	--
Insolubles	0.00	0.00	0.01	0.50	--
CaSO <sub>4</sub>	0.65	0.00	1.69	1.33	--
CaCl <sub>2</sub>	0.73	0.94	0.18	0.06	270.9
MgCl <sub>2</sub>	0.25	0.29	0.16	0.78	71.4
KCl	nd	0.10	--	--	27.1
NaCl	96.00	97.64	97.62	89.67	27.6

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fractional crystallization, whereby most of the calcium and magnesium compounds remain in the residual liquor or "bittern." Salt is produced from sea water by such a method. On concentration of the average oil-field brine, clarified in the manner outlined, to a specific gravity of about 1.200 crystals of calcium sulfate will begin to form. Much of the calcium sulfate present in the brine will have separated before the solution becomes saturated with NaCl and crystals of it begin to form. This fact offers a way for the partial removal of calcium sulfate, if desired. When the concentration of the residual liquor has reached a specific gravity of 1.260 the major portion of the sodium chloride will have crystallized and should

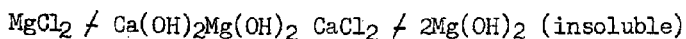
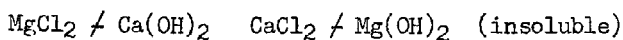
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Notes to Table I:

- (a) This salt is from clarified oil-field brine, using solar means only for evaporation. The salt was raked from the brine at three different concentrations, and all three lots combined for analysis. The residual bittern amounted to approximately 10 percent of the original volume. The salt was not washed, but sucked as dry as possible on suction filter, and then oven dried.
- (b) This salt is from clarified and sulfate-free oil-field brine, and evaporation conducted in pan on laboratory hot-plate. The salt remained in the "mother liquor" until evaporation was complete, then sucked as dry as possible on a suction filter, washed with saturated brine, again sucked dry, then oven dried. The bittern amounted to 8.8 percent of the original volume, and contained 397. grams dissolved solids per liter.

be removed, preferably from a hot solution since under such condition there is not the tendency for the double chloride of magnesium and potassium to crystallize and contaminate the sodium chloride. The salt may be harvested as it forms or left to accumulate until the specific gravity of the residual liquor indicates it is advisable to quit further concentration. If concentration is carried too far, the solution will be viscous and difficult to drain from the crystals. Where the salt has been allowed to accumulate in contact with the bittern, it is usual practice to wash the separated crystals with a portion of clarified and saturated brine to remove adhering bittern. In any event the salt is centrifuged and dried. Table I gives analysis of (a) unwashed salt made by solar evaporation of clarified oil-field brine, (b) washed salt made by pan evaporation of clarified-sulfate free oil-field brine, (c) rock salt,<sup>2</sup> and (d) sea-salt crystals,<sup>2</sup> and also, analysis of bittern from salt (b).

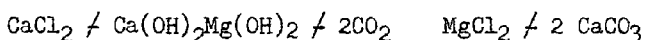
The methods for the utilization of oil-field brine are subject to numerous variations. The variations will depend upon the products desired, their purity and value, and several other factors. For example, it may be desirable to recover the magnesium from the brine in the form of magnesium hydroxide. This may be done in conjunction with the clarification, if the iron, alumina, etc. are not objectionable. Otherwise, it is done following the clarification. The separation of the magnesium as the hydroxide is brought about by addition of the proper amount of "milk of lime" or "milk of dolime". (Dolime is the name for caustic calcined dolomite.) The reactions involved are:



The precipitation of the magnesium hydroxide in a non-gelatinous condition is essential to the

success of this operation, otherwise the rate of filtration is prohibitively slow and washing is unsatisfactory.

Another reason for removal of magnesium prior to evaporation of the brine and crystallization of the salt arises when the residual bittern is to be utilized in the preparation of flake calcium chloride, because the presence of magnesium chloride is detrimental in the majority of the uses of calcium chloride such as curing of concrete and in refrigeration. However, if the bittern is to serve in the preparation of magnesium chloride from dolomite there is no advantage in removing it from the brine at this time. This use of calcium chloride was the basis for several plants constructed during World War II for the production of magnesium chloride for electrolysis to metallic magnesium. The process involves mixing hydrated dolime with calcium chloride solution and introducing carbon dioxide. The reaction takes place according to the following:



The same reaction has been used experimentally in the Oklahoma Geological Survey laboratory, reacting milk of dolime with clarified brine in the presence of carbon dioxide, and yielding a brine in which all or nearly all calcium chloride had been replaced by magnesium chloride.

Sodium chloride crystallized from clarified Oklahoma oil-field brine could serve for many purposes where high purity is not essential. It could also serve in the preparation of high purity solutions and high purity salt. If the "crude" salt is dissolved to yield a saturated solution, and this solution subjected to chemical treatment and filtration, it will then be suitable for use by the alkali industry or for recrystallization to yield a high-purity salt, and at a very reasonable cost. Comparison of the analyses of salt from Oklahoma



oil-field brine and rock salt and sea salt show that the salt obtained from oil-field brine is adaptable to numerous industrial and domestic uses as easily as salt from other sources. The domestic supply for the Pacific Coast and the industrial supply for the Pacific Coast alkali industry are both obtained from sea water. This salt is by no means more acceptable for the purposes than salt from oil-field brine.

A large amount of brine is brought to the surface in the production of petroleum. Whenever there is an appreciable volume it is required that it be disposed of underground in formations that cannot be damaged by it. This surely is conservation of a natural resource but at what a cost. If it could be processed to yield products of commercial value it would be better conservation. Yet, if and when Oklahoma oil-field brine is processed, without much question the brine will be produced for its own value and at locations adapted to the manufacture and distribution of the products.

Market Quotations from the Oil, Paint and Drug Reporter, issue March 17, 1952

Salt, rock, burlap bags, c.l., works \$1.09 cwt.

Table, vacuum, common, fine, \$1.09 cwt.  
bags, c.l., works

Potassium muriate, 50-60%  $K_2O$ , bulk, \$ .42 unit-ton.  
Carlsbad, N. M.

Calcium chloride, flake, 77-80%,  
paper bags, c.l., works \$25.00 tons

solid, 72-75%, drums, c.l. \$23.50 ton.  
frt. equald.

liquid, same basis, 40%, \$10.50 ton.  
tank cars.

Magnesium chloride, anhyd. lumps,  
95-98%; 40 tons

works, frt. equald.           \$ .12 3/4 per  
lb.

Hydrous, flake, l.c.l.,       \$49.00-\$51.00  
works                            ton.

Magnesite calcined, dead burned, \$36.30 ton.  
bulk, c.l. works, Chewalah,  
Wash.

Magnesia, calcined, tech. ctns.   \$ .32-.34 3/4  
works                            per lb.

References:

- 1/ MacMillan, Robert B., Natural Salts and By-Products, Rogers Manual of Industrial Chemistry, Sixth Edition, p. 362.
- 2/ Hou, P. T., The Manufacture of Soda, Rogers Manual of Industrial Chemistry, Sixth Edition, p. 411.

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Are These Fair Questions

A news item in the February issue of Chemical Engineering Progress, published by the American Institute of Chemical Engineers, reports that the Longview (Texas) plant of the Texas Eastman Company began operations in January producing ethanol, n-butyraldehyde, and isobutyraldehyde from natural gas and propane. The plant, a division of Eastman Kodak Company, is located on a 2400 acre site. A portion of the products will be offered for sale but the major portion will be transported to the Eastman plant at Kingsport, Tennessee, for further processing into ethyl alcohol, butyric acid and its

derivatives, acetic acid, plasticizers, and solvents.

Questions come to mind. Does East Texas offer the prospective manufacturer a better, cheaper, or otherwise more advantageous supply of raw material? How much interest have Oklahoma producers of propane and natural gas in such an industry? Is railroad transportation from East Texas more efficient and are the rates lower than those from Oklahoma to that area of the country east of the Mississippi River and west of the Appalachian Mountains?

The item reports further that the Eastman plant is situated on the banks of the Sabine River in Harrison County and about five miles from Longview, and continues (quote) "The Sabine is a small stream during most of the summer months, and because of this, Eastman has created a 300-acre lake on its property by erecting a dam across a small creek. The lake is the shape of a horseshoe and measures about one and one-half miles around from tip to tip. Into one end of the lake river water is pumped as needed. Also into this end of the lake condenser water is discharged from the plant. Water for plant use is taken from the bottom of the other end of the lake. The lake thus provides a settling and cooling basin which will be of particular importance in the summer months when the Sabine, is low, full of silt, and its water is an elevated temperature" (end quote). This quotation would indicate that the industrial water situation in much of Oklahoma is not as serious as we have been led to believe.

Can it be that East Texans are more aggressive, present their proposition more convincingly, and receive better cooperation from their railroads? Or had Oklahomans rather not have these industries?