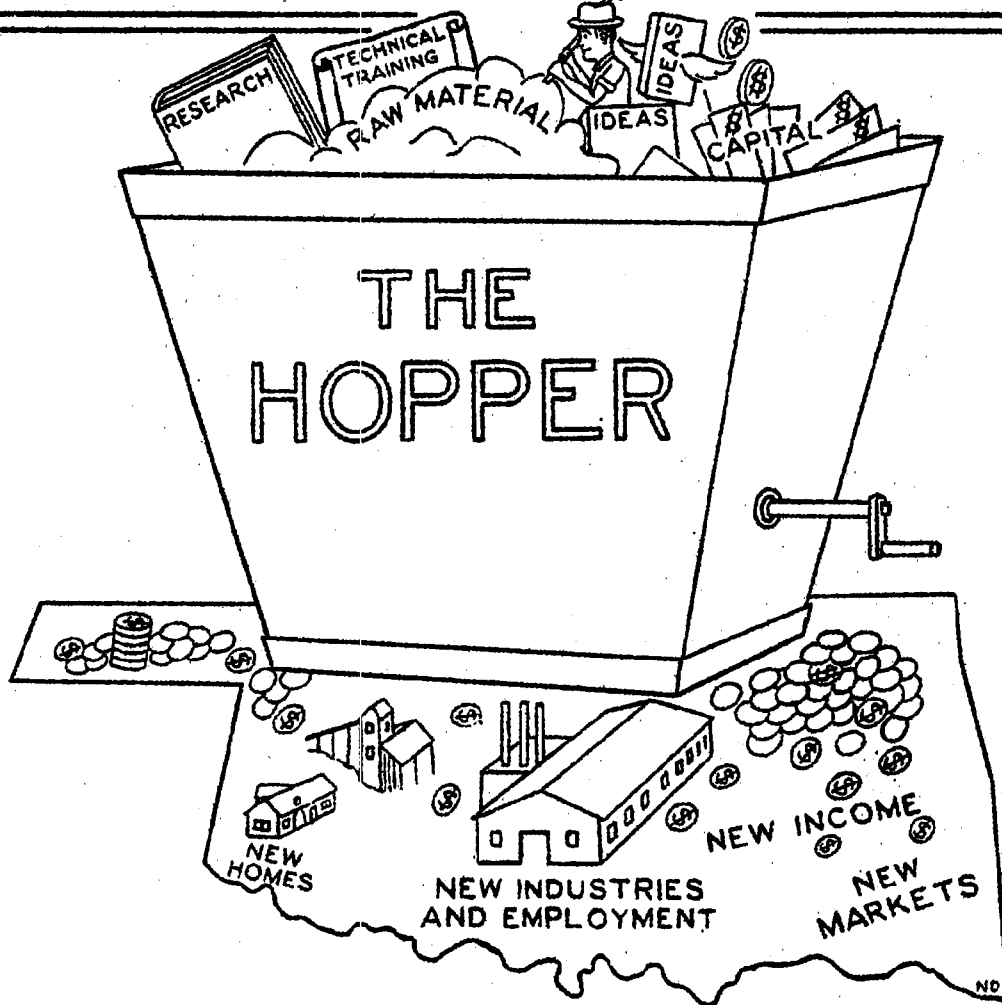


OKLAHOMA MINERAL INDUSTRIES CONFERENCE



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HOPPERATOR'S PAGE

Representatives of brick, tile, pottery, and other ceramic industries of Oklahoma who attended the meeting of the Southwestern division of the American Ceramic Society in Tulsa last week showed considerable concern over the proposal in the State Legislature to add a 2 cent tax to natural gas.

Reason: The whole ceramic industry must use fuel in large quantities. Efforts to attract some of these industries, including glass, and other heavy users of fuel have been making some headway. Abundant low-cost fuel and available raw materials have been good drawing cards.

Two new glass plants and a big rock wool plant, are examples. Other heavy fuel users include the cement and lime plants in the State.

The ceramic men figure they will have to pay the bill through increased fuel prices, and fuel represents between 20 and 25 percent of total manufacturing costs for some of these industries. A 2 cent natural gas tax will represent about 20 percent increase in cost of this fuel to some of these industries, or a net increase in manufacturing cost of around 4 percent, which, they fear, would be a disadvantage in meeting competition from plants in surrounding areas.

EXPERIMENTATION ON INDUSTRIAL USES FOR OKLAHOMA VOLCANIC ASH AND SALT BRINES

By A. L. Burwell, Chemical Engineer
Oklahoma Geological Survey
(Address before the Oklahoma Mineral Industries
Conference at Ada, Oklahoma, November 7, 1946.)

I want to talk to you, and especially to those among you who may enter the manufacturing field, about several close-to-worthless mineral raw materials available in Oklahoma in abundance from which I believe commercial products can be produced economically and for which there appears to be a market.

The first near-worthless raw material about which I wish to talk is volcanic ash--pumicite. This ash is not the result of combustion in the usual sense but the dust ejected by the volcano during eruption and deposited from the air and possibly later transported by water. The deposits look much like bleached-out soil and poor soil at that. Deposits of volcanic ash are known in 24 counties in Oklahoma. The thickness of the deposits range from 1 to 75 feet, the overburden from 0 to 30 feet, and the volume from as little as 500 to as much as 10,000,000 cubic yards.

Noting the tendency of this material to bloat when heated to high temperatures, we have run a series of tests to determine the temperature and temperature range within which the bloating takes place. The loose powder was placed in small porcelain crucibles and ignited at 1090°C. (approximately 2000°F.) for 2 hours. Then we had a small furnace in which we could maintain higher temperatures. With this furnace at 1200°C, we transferred one crucible to it and held it there for 15 minutes. Other crucibles were similarly treated at 1250°, 1300°, and 1350°C. (roughly corresponding to 2200,

2280, 2370, and 2460°F.). In addition, complete analyses were made on many of the samples tested. This represents a great amount of laboratory time. Our object was to see if we could determine the reasons behind the bloating, and why the differences which you observe in the bloated specimens. To go into the subject here would bore most of you to death but I can state the basic fundamentals briefly:

The raw material must have a composition that on heating will develop a high percentage of glass phase. The mass must become thermoplastic on heating and maintain this condition over a satisfactory temperature range. Gas or gases must be generated from and within the mass while in the thermoplastic condition in quantity sufficient to create a cellular structure, and the viscosity of the mass during the thermoplastic stage must be high enough to prevent escape of the gas or gases so as to retain the structure on cooling.

You may be interested, however, in what appear to be the possibilities for commercial exploitation of the process.

Let's examine one of the test series more carefully. After heating at 1090°C., the material is a compact, shrunken, vitrified mass. The color of the original powder was cream white. The mass is now brick red. After heating at 1200°C., the material is grey in color and slightly expanded. Heated at 1250°C., cells are visible and the expansion is greater. At 1300°C., there has been further expansion and the cells are larger. At 1350°C., the highest temperature used, there is real expansion. With the limited equipment at our disposal we produced on a small scale what we believe can be made commercially on a large scale.

This bloated volcanic ash is truly cellular in structure, not merely porous. It is lightweight. It can be made weighing 35 pounds and even less per cubic foot. It will float on water. It is impervious to both liquids and gases. It is strong, amply strong for construction purposes. Am I a screwball when I visualize this cellular material--chemically inert, rot proof, moisture proof, vermin proof--being used in refrigerators, in cold storage plants,--being used for insulation against heat, cold, and sound in homes and factories? Am I a screwball when I visualize slabs of this product 2 to 4 inches in thickness, 2 or more feet wide and 10 feet long being set in channel steel sills and beams, or possibly aluminum rather than steel, all cemented together giving practically monolithic walls, floors and roofs with glassy smooth exterior and rough pitted surface on the interior to better bond the coat of finishing plaster. Nutty as a fruit cake? Perhaps. Still, Oklahoma has plenty of the volcanic ash. She has also the low-cost fuels necessary for its processing. Certainly from our experience of the past summer a home and working place insulated with PUMICELL (that is our name for the product) would have been welcome. What I mean to say is that when Pumicell is manufactured in Oklahoma from Oklahoma materials, Oklahoma and surrounding states will supply a market.

The second near-worthless raw material about which I wish to talk is salt. Extensive beds are known to exist in the western and northwestern parts of the state. Brines carrying salt are known to occur in nearly all parts of the state except the extreme northeastern and southeastern.

Production of Salt in the United States

	<u>1944</u>
Rock Salt, dry mined	3,448,238 tons
Salt, raised as brine	12,263,933 tons
Evaporated for salt	3,942,621 tons
Used as brine	8,326,312 tons

Over three times as much salt is raised as brine as is dry mined. Wells are drilled into salt beds (as deep as 6000 ft. in West Virginia), water is introduced, and saturated brine solution pumped out.

Flowing salt springs occur in western Oklahoma. The principal ones are located (1) along the Cimarron River in Woods, Harper, and Woodward counties, (2) on Salt Creek southeast of Southard in Blaine County, (3) on the North Fork of the Red River south of Carter in Beckham County, (4) on Sandy Creek south of Eldorado in Jackson County, and (5) on the Elm Fork of the Red River in northern Harmon County. These springs are not newly discovered but have been known for years. Nor is the method that I believe feasible for their utilization new. In fact, it is very old. Long before statehood brine from these springs was evaporated for salt. I quote from an old bulletin. "Large tanks or ponds on the floor of the plain. These were built of slabs of rocks. The water is fed into the tanks as desired and as it evaporates a crust of salt forms on the surface which settles to the bottom forming a hard crystalline layer of salt. This layer is broken up with picks and the salt shovelled or raked into piles at the edge of the tanks. A sample of salt taken from the piles analyzed 99.15 percent sodium chloride."

Solar evaporation for the recovery of salt is practised in many parts of the world utilizing brine from wells, springs, lakes, and sea water. The method has reached its highest degree of perfection in California, which ranks sixth among the states in production of salt and where practically all the salt is produced by solar evaporation. A typical plant with 50,000 tons per annum capacity operating on sea water in the San Francisco area will cover 2000 to 3000 acres of which only 75 to 125 acres will be used for crystallizing ponds and the balance for concentrating ponds. Please note that the salt content of sea water is less than 10 pounds per barrel. The stream below the springs in

Blaine County contains 77 pounds per barrel. (The barrel here is the 42 gallon oil-field barrel). It has been estimated that the flow from these springs southeast of Southard amounts to 4000 to 5000 barrels per 24 hour day without any allowance for brine traveling in the sand floor of the stream. I think that any salt man will tell you that this brine is not a difficult one to handle. The success of a plant here or elsewhere in the state will depend partly but not wholly upon the weather, or more explicitly, on the amount of evaporation in excess of rainfall. Therefore, a comparison of the San Francisco area with some western Oklahoma point may be interesting. No figures are available for Southard but we do have figures for Tipton, for comparison.

	<u>Annually</u>
Total evaporation less rainfall for San Francisco	31 to 43 in.
Total evaporation less rainfall for Tipton	31 to 86 in.
Average for past 7 years	53.4 in.

These seven years include the one with the greatest rainfall in 50 years and three others among the top wet years. So, it would appear that solar evaporation can be carried out, but if the method is too slow for our fast-moving industrialists may I suggest that a high-pressure natural gas line supplies the U. S. Gypsum Co. plant at Southard, which is less than 3 airline miles to the northwest, and is on the Frisco railroad.

According to our figures these salt springs could support a plant turning out 150 tons per day (50,000 tons or better per year) but if you do not care for the salt business as such, perhaps you would like to purify this brine and concentrate slightly, then electrolyze to produce caustic soda, hydrogen, and chlorine. Now you are in the chemical business.

Prewar, better than 1 million tons of caustic soda were produced in the United States annually. Over one-half of it was made by electrolysis of salt brine. Rayon and cellulose film were the largest consumers with 230,000 tons; chemicals next with 220,000 tons, and even the petroleum refiner consumed 88,000 tons. Chlorine is used for water purification, for the manufacture of hypochlorites, bleach liquor, chlorates, and chlorinated hydrocarbons of which carbon tetrachloride, tetrachlorethylene, and chloroform are the best known. In some instances, chlorine is re-coupled to the hydrogen to yield hydrochloric acid,--the muriatic acid used in acidizing oil wells, etc. Hydrogen is used, of course, for the "hardening" of oils and fats, making Crisco-type materials from vegetable oils.

Tremendous quantities of brine are consumed in the ammonia-soda alkali works where the principal products are soda ash, "bi-carb", and caustic soda. This industry involves very large investment of capital. If a new plant is to be competitive with existing ones it is going to be a million and a half dollar affair. In sharp contrast, the electrolytic caustic soda plant can operate with a few units and still be on sound economic ground.

Another source material for salt is our oil-field brines which is available in tremendous quantities. Most of you know what is being done with oil-field brines at the present time. It is being handled carefully so as not to disturb its equilibrium and tenderly put back underground with no love lost, as quickly and gingerly as possible, and a heck of a lot of money is spent doing this. You all will do as you please with the stuff. Let me simply tell you what we have done with it in the laboratory and what we got from it, and you will probably then be glad to forget the whole subject.

The contents of brine from the Moore disposal plant southeast of Oklahoma City calculated from analysis is shown in pounds per 42 gallon barrel:

Sodium chloride (NaCl)	55.5 pounds
Calcium chloride (CaCl ₂)	11.75 pounds
Magnesium chloride (MgCl ₂)	2.5 pounds
Calcium sulfate (CaSO ₄)	3.5 ounces
Calcium carbonate (CaCO ₃)	0.4 ounces

This is a strong brine as oil-field brines run. However, for our experimental work we selected a brine from the Fitts pool because it is representative of the average oil-field brine of the state. The composition after clarification is:

(Pounds per 42 gallon barrel)	
Sodium chloride (NaCl)	45.0 pounds
Calcium chloride (CaCl ₂)	9.25 pounds
Magnesium chloride (MgCl ₂)	2.75 pounds
Potassium chloride (KCl)	14.5 ounces
Calcium sulfate (CaSO ₄)	1.75 ounces
Strontium sulfate (SrSO ₄)	3.0 ounces

Our first operation was to clarify the crude, dirty-looking, ill-smelling brine which was brought about by adding approximately 1½ ounces of hydrated lime per barrel of brine. This raised the pH to a point where the dissolved iron would separate. Aeration followed, then sedimentation where the iron floc settles out dragging down suspended matter and some oil. From the clear well the brine passes through a rapid sand filter, similar in construction to that used in your municipal water works but much smaller. Two filters, each 200 square feet in area will handle, if used alternately, 1000 barrels per day.

We have allowed some of this clarified brine to evaporate naturally, that is by exposure to the air only. The crude salt harvested is as good as most crude salts. If handled as the California

crude salt no difficulty will be experienced in obtaining 99.9 percent purity in re-crystallized salt.

Crude Salt by Solar Evaporation of Clarified Brine

Sodium chloride (NaCl)	96.16 percent
Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)	1.76 percent
Magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	0.54 percent
Moisture	1.65 percent

71 Barrels Bittern from 1,000 Barrels of Brine contains:

Calcium chloride (CaCl_2)	763 pounds
Magnesium chloride (MgCl_2)	237 pounds
Potassium chloride (KCl)	32 pounds
Sodium chloride (NaCl)	65 pounds
Sp. Gr. -----	1.300

Also, we have worked on a combination process for the utilization of dolomite, a low-value mineral, and this clarified brine. You can follow the clarification process from the well to the storage. At the same time, we burn dolomite to caustic dolime. Dolomite, as most of you know, is a double carbonate of calcium and magnesium, so our product on burning is carbon dioxide and a mixture of lime and magnesia (dolime). The dolime is slaked, preferably under pressure, but we obtained comparable results with near complete hydration of the lime and magnesia by holding the slaked mass at 35°C. for three days. The calculated quantity of the slaked dolime in the form of a slurry is run into a rotating drum which is air-tight except for release or control valve. In the meantime the flue gases are scrubbed and CO_2 absorbed and regenerated in a manner similar to that used at your dry-ice plant here in Ada, and the gas passed into the rotating drum until tests indicate the proper amount has been taken up, with the conversion of all the calcium from both the dolime and the brine into calcium carbonate (precipitated chalk) and the replacement of the calcium chloride by magnesium chloride

in the brine. The chalk is removed, washed, dried, and sold as such or burned to powdered quicklime. Now, the brine contains salt, considerable magnesium chloride, and a little potassium chloride. The solution is concentrated to saturation, soda ash in solution is run into the brine in slight excess of the theoretical requirements, and the mixture agitated. By holding the solution at saturation and maintaining at the boiling point approximately all magnesium will separate as basic magnesium carbonate, the 85 percent magnesia of the trade, which is used as insulation, especially for steam and refrigeration line covering, and for medicinal purposes. After removing the precipitate, it is washed and dried. The hot liquor is then ready to go to grainers, or other type of evaporators and will yield high-purity salt, or the liquor can be run to storage to be used as needed for electrolysis. This flow sheet is not a fixed procedure. It can be changed to meet changed requirements. But it does contain an idea for the fellow who is looking for one.

So much for our experiments on salt brines, and for what we think can be made from salt, either from salt beds, salt springs, or oil-field brines. Suppose salt is produced from our raw materials, how about the markets? What about competition? There are others more competent than I to deal with this subject--men like Prof. Vaughan of the University of Oklahoma, who is an expert on the subject of marketing whereas I am a guesser. There is no harm in guessing so long as it is recognized as a guess and nothing more. In this case, instead of playing a hunch I stake my guess on a paper carton of high-quality table salt I purchased at a grocery store in Norman. The salt apparently was not made in Kansas. They produce, you know, a large tonnage of salt in Kansas from the same formation which is an extension of the beds found in western Oklahoma. No, not Kansas. It is put out by the White Salt Company of San Francisco, California.

OKLAHOMA INDUSTRIAL TOUR
June 26 - July 12

Although the mountain could not be moved to Mohammed, an Oklahoma Industrial Tour now being organized will take samples of the mountain of Oklahoma Industrial Opportunities to the north-eastern United States, June 26-July 12. The tour is being designed for the purpose of showing as much as possible of the raw materials and other favorable factors that Oklahoma offers.

The tour exhibits and the group making the trip will occupy a special train, with present indications that a second special train may be necessary because of the large number who have expressed a desire to make the tour. Although the committee has not started soliciting reservations for the trip, enough requests have been received already to about fill the available space on the train that will carry the exhibit. Factors influencing industrial development, and Oklahoma's position in relation to these factors, will be displayed. The factors to be shown by specimens, charts and maps, are:

- Oklahoma's location and position in the U. S.
- Favorable competitive position, proximity to markets
- Distribution facilities
- Transportation facilities
- Labor
- Industrial fuel
- Power
- Water
- Location of production materials
- Research
- Compatible laws and law trends, reasonable tax rates
- Sites, industrial foundations, buildings available, and space
- Living conditions, climate, recreational facilities, etc.