

Oklahoma Geology Notes



INDUSTRIAL WATER

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The suitability of water for steam production is determined on its tendency to foam, to cause corrosion, and to scale. Foaming is usually attributed to the presence of sodium and potassium salts. Therefore, when the concentration of these compounds reaches the point where foaming becomes bothersome, the remedy is to blow off some of the concentrated water and to replace with fresh water. In the event that suspended matter is increasing the tendency to foam, the remedy will depend on whether the suspended matter was present in the water before it entered the boiler or came from deposition resulting from the influence of heat on the soluble matter. Corrosion by water is generally due to acid formed by the hydrolysis of dissolved salts, notably the chloride and sulfate of magnesium. Dissolved gas is also troublesome. Corrosion may be caused by carbon dioxide, hydrogen sulfide, and oxygen. Scale is a product of both suspended and dissolved matter, and is of several different types depending upon the nature of the scale-forming ingredients.

Water for use in heat exchange is examined for the presence of the same impurities as for steam production but their importance is relatively less. In some instances the presence of organic matter and biological growth are of more importance than the presence of inorganic matter.

Water for processing may have to conform to critical specifications, and the specifications may cover wide range. Most processing water must be free from suspended matter. Many processes demand freedom from iron. Others stress sterility but certain of these may find certain dissolved salts beneficial, as in brewing. Other processors will accept rather high concentrations of dissolved salts beneficial, as in brewing. Other processors will accept rather high concentrations of dissolved salts if the effects of such impurities may be controlled or eliminated by the addition of certain sequestering agents or chelating compounds. At the other extreme are processes requiring water free from all impurities and sterile, among which the manufacture of pharmaceuticals is a prominent example.

Water Treatment

Obviously the methods of purification or the type of treatment will depend not only on the composition of the water but upon the intended use as well. Included in the various methods are both physical and chemical ones and combinations of both kinds. Volatile and oxidizable impurities are removed by aeration in fountain, spray, or cascade. The removal of hydrogen sulfide and of ferrous iron are examples. Suspended matter, which may include bacteria and micro-plant growth as well as silt and clay, is removed by sedimentation, or by coagulation and filtration, or by filtration alone. Residual micro-organisms are killed by chem-

ical or other sterilization. Soluble impurities are rendered innocuous by addition of sequestering agents, or are removed by pre-heating, or by chemical treatment such as lime-soda, or ion exchange, or by distillation.

In order to understand the problems of water treatment, it is necessary to examine each type of method mentioned above. All natural waters contain dissolved gases such as oxygen, nitrogen, and carbon dioxide and frequently certain other undesirable gases and may have odor derived from decomposing matter in the water which may be removed by aeration. If iron is present in the water in ferrous condition aeration oxidizes it and with controlled alkalinity it precipitates. Spraying and trickle towers are two methods generally recommended for aeration of industrial waters.

For the removal of suspended matter, including turbidity from organic as well as inorganic matter, probably the method first used and still used where circumstances warrant, is settling in reservoirs of sufficient size and depth. When such impounding is not suitable or is too slow, the process may be hastened and improved by the addition of chemical coagulants such as salts of iron and aluminum. The floc formed by the hydrolysis of these salts settles and drags the suspended matter with it. When the settling alone is too slow or incomplete, filtration must be resorted to. There are several types of filtration including slow-sand and rapid-sand filtration, and also in certain instances, mechanical filtration using some type of filter-press.

For industrial use, it is often necessary to remove the dissolved solids entirely or in part, or to change the character or composition so that it is less troublesome or less harmful. Where more or less complete removal of the dissolved solids is demanded recourse is had to ion exchange methods, wherein the cations (calcium, magnesium, sodium) are first absorbed by a suitable "exchanger" and then the anions (chloride, sulfate) are absorbed by contact with another type of "exchanger." If only a change in composition is necessary to meet the user's specifications, it may be attained in several ways. Suppose the undesirable dissolved solid is magnesium sulfate and that sodium sulfate is not detrimental, a base exchange (zeolite) method might be employed which would remove the magnesium and replace it with sodium. Of course, it is seldom that a water will contain only a single compound. As a matter of fact, many waters contain a complex mixture of soluble matter.

A typical "hard" water might be found on analysis to contain calcium, magnesium, and iron in solution as bicarbonates, chlorides, sulfates, and nitrates. The more or less standard treatment for such water would be the lime-soda ash process which involves the use of lime, either quicklime or hydrated lime, to cause precipitation of the calcium as carbonate and the magnesium and iron as hydroxides, and the use of soda ash (sodium carbonate) to remove soluble calcium which might be present as sulfate, chloride, or nitrate after the lime treatment. Obviously this treatment does

not remove all dissolved solids, since molecular equivalents of the original sulfate, chloride, and nitrate will remain in solution as sodium salts which are less objectionable than their calcium and magnesium counterparts. If the water is destined for use in a boiler, this lime-soda ash process usually would be followed, but if the water is to serve for certain other purposes it might be feasible and more economical simply to sequester the objectionable "hardness" and hold it in solution. Several alkali "dehydrated" phosphates are recommended, of which the sodium hexametaphosphate is the best known. Another means of rendering certain impurities innocuous is called "chelating." The reagents employed usually are polyamine polycarboxylic acids, the best known being ethylene diamine tetra acetic acid, which form complex metallic ion compounds. Such complex ions cannot be precipitated by the chemicals usually employed for that purpose.

Treating of water for industrial use is much too complicated to be covered satisfactorily in the short space allotted here. If the statement that the lime-sodash process is usually followed in treating hard water for boiler-feed is questioned the writer would have to wsh because there is a growing tendency simply to control the pH by addition of sulfuric acid, but one should not attempt it unless he knows what he is doing. After all, preparing water for industrial use is both an art and a science, with the chemist an essential part of the team.

OKLAHOMA HIGH NATIONALLY IN PRODUCTION OF MINERAL RESOURCES

Just released by the U. S. Department of Commerce are the results of the 1954 Census of Mineral Industries, conducted jointly by the Bureau of the Census and U. S. Bureau of Mines. The thirteenth mineral census since their beginning early in the twentieth century, the 1954 report shows Oklahoma to be in 5th place nationally in value of minerals produced, following Texas, California, Louisiana, and Pennsylvania, but ahead of West Virginia, Illinois, Kansas, New Mexico, and Kentucky. Each of these first ten states is a major producer of the mineral fuels—petroleum, natural gas, and coal.

Oklahoma was fourth in value of crude petroleum and natural gas extraction, a position she has held for many years. But, surprisingly, Oklahoma is second nationally in number of employees in the oil and gas industry, ranked only behind Texas, a rank which evidently is a reflection of intense developmental work as compared with other oil-producing states.

Bureau of Census data show mineral production in the United States in 1954 valued at \$14.8 billions. During this year Oklahoma contributed 4.98 percent of the national total by producing minerals valued at \$737 millions, of which petroleum and natural gas accounted for \$697.3 millions; nonmetallic minerals, \$12.1 millions; and metallic minerals-bituminous coal, \$27.7 millions. In this mineral extraction and development, 36,000 employees worked 60 million hours for which they received \$151 millions.

Mineral-rich Oklahoma, which has produced more oil per acre than any other state in the nation, is truly grateful for its petroleum and natural gas. Together they made up 94.6 percent of our total 1954 mineral production value. WEH

WHAT ABOUT LIGHTWEIGHT AGGREGATE?

The lightweight aggregate industry is relatively new. Back in 1920 only a minor amount of lightweight aggregate was used. By 1947 the consumption had increased to 6,150,000 cubic yards for the year and by 1954 it had further increased to 26,750,000 cubic yards for the year. Still greater consumption is predicted. ¹(1956) Naturally, a minerals industry growing like this deserves our attention.

A lightweight aggregate has been defined "as an aggregation of fine and coarse particles of a material which because of its light weight, strength, low absorption, and chemical stability, can be mixed with cement to form a concrete of pre-determined characteristics. ²(1954) This definition ignores the use of lightweight aggregation in compositions other than concrete. For years, crushed cinders was the principal lightweight aggregate, with granular pumice being utilized in certain areas. The cement referred to in the above definition probably means portland cement, that being the most widely used cement. However, the term concrete is used in too restricted a sense. Even the definition of concrete as given in Webster's International Dictionary (1942), "artificial stone made by mixing cement and sand with gravel, broken stone, or other aggregate" does not seem adequate as the word is currently used. As a matter of fact, the earliest known concrete, made more than 2,000 years ago, was not made from cement but from hydraulic lime, and still can be where hydraulic lime is available. Further, the definition ignores the constantly increasing use of bituminous concrete in which asphaltic materials are the binders.

Lightweight materials presently used as aggregate in concrete include natural mineral materials, byproduct materials, and artificial materials. The principal natural materials are pumice and scoria. Byproduct materials that find extensive use are coal cinders and "foamed" blast furnace slag. Artificial materials include products made from clays, shales, slates, certain soils, vermiculite, and volcanic glasses such as perite, obsidian, and volcanic ash.

In spite of the large tonnage of lightweight aggregate used, there are still no satisfactory specifications covering most of the materials. Probably no generalized specifications can be formulated, but rather it will be necessary to make separate specifications for aggregate from each raw material and also for aggregate prepared by different methods from any particular raw material. For example, lightweight aggregate from clay and shale is of two distinct types, namely, the "coated" type and the sinter

type. The coated-type process and products has been described as follows:

“The coated type aggregate is made by rapid firing in a rotary kiln. Gases released from within the clay or shale during the pyroplastic condition causes it to expand into light, cellular particles. The particles are usually well rounded owing partly to the bloating action and partly to the tumbling taking place in the kiln. The quantity and quality of the fluxes in the shale allow this expansion or bloating to take place at a temperature below that at which the particles become sticky so that the product is discharged from the kiln in individual, coated particles. An ideally coated aggregate requires no crushing after firing to supply the required grade sizes.” ² (1954)

The sinter type aggregate may be made in a rotary kiln but is more often made in a sintering machine. In either case, the product is crushed to supply the desired grade sizes, the nature of the raw material and the processing being such that, when plastic, the particles agglomerate and form a clinker. The sintering machine has the advantage that a wider range of raw material may be used but the product does not possess the high strength-to-weight ratio, the good workability, nor the low absorption of the coated type product.

The consumption of lightweight aggregate at the present time is mainly in the manufacture of building blocks. There is also an increasing demand for it for the manufacture of precast forms and shapes for use in construction. A potentially larger use than either of these is for monolithic structural concrete and for bituminous concrete highway construction. It has already been demonstrated that structures such as buildings and bridges in which lightweight aggregate is used require much less supporting steel, thereby reducing the cost materially. Other favorable factors are greater toughness of the concrete, lower thermal conductivity, and improved fire resistance. As an illustration of the advantage to be derived from the use of lightweight aggregate, in the construction of the Tacoma Narrows bridge it is reported that the floor weight was reduced by 2,060 tons, which resulted in a saving in structural steel of over 360 tons and over 360 tons in suspension cables and wire, an overall saving of \$320,000. Another illustration is reported in the construction of a Los Angeles hotel where the use of “50,000 cubic yards of manufactured lightweight aggregate reduced the dead load of the structure by 37,000 tons,” resulting in a 15 percent saving on structural steel. ¹ (1956)

Normally, the particular kind of lightweight aggregate consumed in any area will depend upon its availability, that is, the occurrence of the raw material near the major point of consumption of the product. Other factors are cost of transportation on both raw materials and lightweight product, and the kind and cost of fuel. Where there are natural occurrences of pumice and scoria it would be expected that they will be the dominate light-

weight aggregates, and where byproduct cinders or "foamed" blast furnace slag are being produced such product will be used. In these instances the difference in cost would not warrant use of a superior product even if it could be obtained. Of course, there are certain specialty lightweight aggregates, such as expanded perlite and exfoliated vermiculite, where high transportation costs on the raw material are offset by other considerations.

To date, no naturally occurring lightweight aggregate is produced in Oklahoma. Economic considerations indicate that production will depend upon clay, shale, and volcanic ash as raw material for lightweight aggregate. It is possible that expanded volcanic ash may in some instances be able to replace expanded perlite. (1949) A plant at Hutchinson, Kansas is producing a "popped" volcanic ash product in a small way. However, the main reliance will fall without doubt on clay and shale.

Investigations have been made in the laboratory of the Oklahoma Geological Survey during past years on the bloating properties of Oklahoma clays and shales. Mineral Report 24 (1954) gives the results obtained on six shales from Pennsylvanian-age formations in the northeastern part of the state. Under proper conditions of time and temperature all six will yield bloated aggregate of the coated type. A later report in the Proceedings of the Oklahoma Academy of Science (1954) deals with a shale from the Hilltop formation, also of Pennsylvanian age, in Seminole County from which a satisfactory coated-type product was obtained. Preliminary tests indicate that a phosphatic shale which occurs immediately below the Welden limestone in Pontotoc County has strong bloating properties. Tests on shales from Cleveland, Oklahoma, and Tillman counties, all from Hennessey formation, and using the bloating procedure followed in this laboratory yielded negative results. This is not surprising since the State Geological Survey of Kansas had obtained similar results on Permian-age shales, and had suggested that such shales might possibly be converted to lightweight aggregate by sintering. (1951) Sintering is usually produced by mixing pulverized shale with coal or petroleum oil and igniting, the process being carried out on a traveling grating. A clay from section 2, Township 14 N., Range 24 W., near Cheyenne in Roger Mills County had strong bloating properties, as did similar clays from Beaver and Woodward counties. However, tests indicated that all had short bloating range, so that sintering probably would be the preferred process.

In Oklahoma there are currently only two producers of manufactured lightweight aggregate, one in Tulsa County utilizing a Pennsylvanian-age shale and the other in Oklahoma County utilizing an alluvial clay-bearing soil. Such alluvial soils and especially loess from certain areas have been found to yield satisfactory sinter-type material.

It may be of interest to compare the tonnage consumed in the U. S. of the usual concrete aggregates, such as sand, gravel, and

crushed stone, with the tonnage of some of the lightweight aggregates, such as expanded slag, pumice and expanded perlite, since it will illustrate the relatively small proportion of the concrete aggregate business as yet taken by the lightweight materials. However, comparisons based on tonnage figures are hardly justified because of the differences in bulk density. Comparison on a cubic yard basis would be more appropriate, but figures on a tonnage basis are the only ones available.

The figures given herein are for sand, gravel, and crushed stone used for concrete and road metal only, whereas the figures for expanded slag and pumice are for concrete only, and the figures on crude perlite and expanded perlite are for all uses which include the products concrete, plaster and wallboard. All figures given are approximate and are on the basis of 1952 and 1953 reports.

Sand	157,000,000 tons	valued at about	\$ 0.95 ton.
Gravel	280,000,000 tons	" " "	\$ 0.73 ton.
Crushed stone	187,000,000 tons	" " "	\$ 1.30 ton.
Perlite, crude	200,000 tons	" " "	\$ 7.25 ton.
Perlite, expanded	175,000 tons	" " "	\$51.00 ton.
Pumice	555,000 tons	" " "	\$ 2.75 ton.
Slag, expanded	2,290,000 tons	" " "	\$ 2.45 ton.
Cinders	(figures not available)		

With shale suitable for the manufacture of lightweight aggregate worth about \$1.50 per ton at the quarry it would seem that processors of both the sinter-type and the coated-type aggregate have ample opportunity in the Oklahoma area when the advantages to be derived from their use are considered, together with the availability of abundant low-cost fuel with which to do the processing. Attention is especially directed to expected advantages to be had in bituminous road construction, such as prevention of "creeping" of the concrete and development of highly skid-resistant surface. Development along this line would make our present facilities entirely inadequate. ¹(1956) A.L.B.

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