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MATERIALS FOR POZZOLAN:
A REPORT FOR THE ENGINEERING GEOLOGIST*
(An abstract)

Introduction

Originally, pozzolan materials were the volcanic tuffs and ashes quarried, for use in mortars, in the vicinity of Pozzuoli, Italy, from whence came the name: pozzolan. Builders in the Roman times had discovered that these volcanic substances produced stronger and more durable mortars than did admixtures of ordinary sand. It was also found that, where volcanic tuffs and ashes were not available, ground tile, brick, and pottery served as satisfactory substitutes for pozzolan. In recent times, other natural or artificial substances have been used for this purpose.

Thus, today the term "pozzolan" covers a wide range of substances that can be defined as: "siliceous materials which, though not cementitious in themselves, contain constituents which at ordinary temperatures will combine with lime in the presence of water to form compounds that have a low solubility and possess cementing properties." Materials used for pozzolans may be divided into four groups: (1) volcanic tuffs, (2) siliceous sedimentary rocks, (3) burnt clays and shales, and (4) industrial by-products.

Properties of pozzolans

It has been known for some sixty years that several benefits can be derived by admixture of a suitable pozzolan with portland cement, particularly for use in hydraulic structures, the optimum proportion of pozzolan usually being between 10 and 30 percent by weight of the portland-pozzolan cement. The benefits derived are: (1) alkali-aggregate reaction can be greatly retarded or prevented; (2) resistance of concrete to attack by sulfate-carrying waters can be increased greatly; (3) heat generation in massive structures can be reduced; (4) savings in portland cement can be made; (5) cost of the cement constituent may be reduced; (6) tensile strength of concrete can be increased; (7) permeability of concrete can be reduced; and (8) properties of the mix before hardening, such as workability and tendency to segregation and water gain, can be improved. Concomitantly, certain adverse qualities may be introduced into the concrete. Water requirement usually will be increased, although the increase may be unnecessary if air entrainment is employed. Drying shrinkage usually will be increased; and compressive strength and freezing and thawing durability of normal mixes may be reduced.

The mechanism by which the pozzolan accomplishes these changes in the properties of concrete is not fully known. However, the pozzolanic action generally is believed to be in part physical and in part chemical. The physical effects relate particularly to the low

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specific gravity of most pozzolans (ranging generally from 2.3 to 2.8, in contrast to about 3.1 for portland cement), as a result of which the pozzolan occupies a greater volume than the weight-equivalent of portland cement. Thus, if the cement-to-aggregate ratio by weight is held constant, use of a portland-pozzolan cement effectively increases the volume of cement in the concrete, with resulting tendency to increased workability, plasticity, and water requirement.

Chemically, pozzolans decrease susceptibility of the hydrated portland cement to dissolution or deterioration by reaction with the calcium hydroxide released by hydration of the portland cement. Reactive aluminous and siliceous compounds produced by calcination of clays are converted by this reaction with calcium hydroxide into comparatively stable substances, many of which are cementitious. Through destruction of the readily dissolved and decomposed calcium hydroxide, the concrete is rendered less susceptible to leaching or to decomposition by aggressive waters. Also, because the pozzolanic reactions proceed slowly, portland-pozzolan cement concretes harden slowly, and usually, but not always, increase progressively in strength and durability for long periods of time. Those pozzolans which inhibit or prevent cement-aggregate reaction in concrete do so by combination with the alkalies (Na_2O and K_2O) released by the hydrating portland cement. The alkalies thus retained by the pozzolan are unable to attack the aggregate.

Materials used as pozzolans

Materials which can be used as pozzolanic admixtures or replacements of portland cement include:

1. Volcanic tuffs and ashes, including pumicites, of rhyolitic and trachytic and possibly dacitic and andesitic types, particularly those which are hydrothermally altered.
2. Siliceous sedimentary rocks, especially opaline shales and cherts and diatomaceous earth.
3. Clays and shales to be calcined at temperatures in the range 900° F. to 1,800° F.
4. Industrial products, such as fly ash, blast furnace slag, and powdered brick.

1. Volcanic pozzolans

(a) Tuffs and ashes

The volcanic tuffs used as pozzolans occur as porous, consolidated or unconsolidated materials which commonly show evidences of chemical alteration by hydrothermal action subsequent to deposition. The rocks are alkaline or acidic types with SiO_2 content generally ranging from 46 to 72 percent. Volcanic pozzolans are commonly used without heat treatment, but investigations indicate that burning at low temperatures (up to 1,300° F.) is beneficial for some materials. Heating at temperatures higher than 1,850° F. usually greatly reduces activity.

The first large use in the United States of volcanic tuff for portland-pozzolan cement occurred in 1910-1912 when equal parts by volume of portland cement and a deeply altered rhyolite tuff were used in the construction of the Los Angeles Aqueduct for a reported saving of \$700,000 over the cost of straight portland cement. The tuff used in this construction came from deposits at Monolith, Haiwee, and Fairmont, California. Samples obtained from the Monolith deposit are characterized by a fine-grained matrix of completely decomposed volcanic glass and fragmental rock and mineral particles. An estimated composition indicates the tuff to be about 80 percent zeolite (clinoptilolite, a silica-rich heulandite), 15 percent montmorillonite-type clay, and 5 percent quartz, orthoclase, plagioclase, and other minerals.

As determined by experience, as well as by laboratory investigation prior to construction of the Aqueduct, use of the portland-tuff cement increased tensile strength and decreased compressive strength of normal mixes, but increased compressive strength of lean mixes, slowed the rate of hardening so that forms had to be left in place about one-third longer, decreased perviousness, and reduced costs through economies in transportation and purchase.

(b) Pumicite

Pumicite, particularly the Fresno pumicite, has been used widely in concrete construction in California. In most ways this pumicite produces a portland-pozzolan cement similar to that produced by the tuff used for the Los Angeles Aqueduct, except that it is somewhat superior in strength development.

In laboratory tests on 21 rhyolite pumicites by the Bureau of Reclamation, calcination (at 1,400° F.) of the pumicites increased their pozzolanic activity, the improvement in strength development of portland cement-pumicite mortars being especially pronounced when the pumicite contained significant proportions of clay. Most of the clay in these pumicites tested are the kaolinite-type or montmorillonite-type, and were derived from decomposition of the glass shards in the pumicite, probably through the action of volcanic gases rather than by weathering.

2. Siliceous sedimentary pozzolans

(a) Opaline shales and cherts

Siliceous (opaline) shales and cherts, such as those occurring in the Monterey formation in western and southern California, have been used successfully as pozzolan, especially for a chemically resistant cement in marine construction, (as in portions of the San Francisco-Oakland Bay Bridge and in piers of the Golden Gate Bridge). Tests of concrete cylinders up to one year and of pavement cores up to two years indicate satisfactory strength for the concrete containing the high-silica cement; and laboratory and field tests of the cement indicate superior resistance to sulfate attack.

In the Monterey and Puente shales, used for marine construction in California, opal constitutes up to 50 percent and montmorillonite-type clay (beidellite) about 5 to 10 percent of the material.

(b) Diatomaceous earth

Diatomaceous earths have been tested repeatedly as possible sources of pozzolan in the United States. As a group, they are the most reactive with lime of all natural substances. Compressive strength is outstandingly high, both in lime mortar and in portland-pozzolan cement mortar and concrete. Tensile strength of portland-pozzolan mortar is considerably higher than that of equivalent portland cement mortar. Most important, resistance of the portland-pozzolan cement to attack by a 10-percent solution of sodium sulfate may be more than 6 times greater than that of straight high-lime portland cement. However, the one great deficiency of diatomaceous earth as a pozzolan is high water requirement for mixing and, hence, very high drying shrinkage of the concrete containing the portland-pozzolan cement; however, recent research suggests that the excessive water requirement may be controlled by use of wetting agents. By calcination at 1,450° F., the quality of diatomaceous earth pozzolan is considerably improved. Strength development, resistance to sodium sulfate solution, and grindability are increased, and water requirement and drying shrinkage are reduced.

3. Clays and shales (calcined)

Because of the widespread occurrence of suitable raw materials, burned clays and shales are more available than volcanic pozzolans or pozzolans produced from siliceous sedimentary rocks.

Suitable raw materials must be highly argillaceous, the activity usually increasing with clay content. The clays may be kaolinitic or montmorillonite-type, or rarer types such as paligorskite (attapulgitite). The pozzolanic properties are induced by calcination to about 900° F., the optimum temperature of burning generally ranging from 1,300° F. to 1,475° F. By calcination at higher temperatures, the activity is reduced, and becomes very low after calcination above temperatures in the range 1,650° F. to 1,800° F., as the result of recrystallization with formation of more stable compounds. Consequently, powdered brick is a less effective pozzolan than that produced by burning the raw materials at medium temperatures.

Clays and shales used as pozzolans usually contain 50 to 65 percent SiO_2 and 17 to 38 percent Al_2O_3 . Pozzolanic quality generally increases with increased alumina content of clay, suggesting that an aluminous compound produced by calcination in the range 950° F. to 1,650° F. plays a critical role in the pozzolanic reaction with lime. In this connection, it may be noted that burned bauxite forms an excellent pozzolan. Because of the critical influence of temperature of calcination on the properties of clays, production must be carefully controlled to obtain a uniform pozzolan.

The properties of mortar and concrete containing clay and shale pozzolans are widely variable, depending upon the composition and treatment of the pozzolan before use. Some clays and shales show satisfactory strength in lime mortar even without calcination, although calcination almost invariably will improve strength and resistance to sulfate attack and decrease water requirement.

Water requirement for portland-pozzolan cements containing calcined clay is considerably less than that of cements containing diatomaceous earth or shale, and commonly is less than that of cements containing volcanic pozzolans but is nevertheless more than that of straight portland cement. For this reason, drying shrinkage of mortar or concrete usually is increased by use of calcined clay with portland cement, but not so much as if volcanic or diatomaceous pozzolans are used. Heat of hydration of cement usually is reduced by use of calcined clay pozzolan. Durability in freezing and thawing, and wetting and drying, may not be affected by use of a calcined clay pozzolan with portland cement. Spent oil shales calcined after completion of distillation have yielded suitable pozzolanic materials.

Pozzolan for the portland-pozzolan cement was used in the construction of Bonneville spillway dam and fishways at Bonneville, Oregon. The pozzolan component, containing 68 percent SiO_2 and 3.5 percent CaO , was obtained by dredging from San Francisco Bay. The material was calcined at 1,650° F., and the cement was then prepared by intergrinding a modified portland cement clinker with the calcined material in proportions 3 to 1 by weight. The portland-pozzolan cement was significantly lower in cost than the standard portland cement used in construction of the Bonneville powerhouse and locks. After a comparison of the finished portland cement concrete in the powerhouse and the portland-pozzolan cement concrete in the fishway structures, it was concluded that the portland-pozzolan cement concrete showed no cracks or checks and no leakage, and that evidences of segregation were lacking, whereas the portland cement concrete is cracked, some of the cracks being of considerable width, and shows numerous sand streaks and signs of segregation.

4. Industrial products

Products of industrial processes, such as flue dust from power plants (fly ash), blast furnace slag, and powdered brick, have been used as sources of pozzolanic materials. However, they will not be discussed here because the geologist will be little concerned with location of such materials or with the determination of their properties.

Pozzolans and alkali-aggregate reaction

In recent years the discovery has been made that some rocks and minerals of aggregate react with alkalis released during hydration of portland cement and can cause rapid deterioration of concrete. Investigations in the field and laboratory proved the deterioration was effected by development of osmotic pressure in bodies of alkalic silica gel produced from the substance of the susceptible aggregate particles by attack of the alkalis.

Further investigations proved that some siliceous materials would reduce or virtually eliminate expansion of mortar due to alkali-aggregate reaction, if the siliceous materials were finely ground and added to the mix as a replacement of 10 or 20 percent of the portland cement.

At present, the pozzolans known to control alkali-aggregate reaction in concrete and mortar include:

1. Aluminous and siliceous amorphous substances, such as some opals and highly opaline rock types; certain rhyolitic volcanic glasses; diatomaceous earth; kaolinite calcined at 1,000° F. to 1,800° F.; some less common calcined clays, such as paligorskite; and some artificial siliceous glasses, such as Pyrex glass and silica fume, the latter being a by-product of magnesium production. Available data indicate that a material containing kaolinite as the only active ingredient will not pass the mortar test unless the raw material contains more than 75 percent by weight of kaolin, and is subjected to calcination at temperatures in the range of 1,000° F. to 1,800° F. Some fly ashes significantly reduce the expansion of mortars due to alkali-aggregate reaction, but others do not.
2. Many opals and opaline cherts yielding a partial X-ray, powder-diffraction pattern of beta-cristobalite.
3. Calcined (at about 1,400° F.) clays of montmorillonite-type (probably beidellite) commonly inseparably admixed with cristobalite, and which show contraction of the atomic lattice as a result of calcination at 800° F. or 1,000° F. Continued research may indicate the suitability of other clays of the montmorillonite or illite (hydromica) groups.

All of the materials which pass the mortar expansion test also meet the requirements of the test for compressive strength of lime mortar.

Because of the relatively few types of pozzolans which will satisfactorily control alkali-aggregate reaction, the search for pozzolans to be used at a specific project is simplified if alkali-aggregate reaction is not a problem. Thus, since the aggregate is not deleteriously reactive with cement alkalis, the fly ash selected for use as a pozzolan at Hungry Horse Dam, Montana, was not required to pass mortar expansion and chemical tests such as were devised for selection of a pozzolan for use at Davis Dam, Arizona-Nevada, where the concrete aggregate used caused a high expansion. In other instances, use of low-alkali cements may so reduce the possibility of alkali-aggregate reaction in concrete that a pozzolan exerting only moderate control over alkali-aggregate reaction can be used safely, even though the aggregates are deleteriously reactive. At Canyon Ferry Dam, specifications permit use of fly ash with low alkali cement, although the aggregates are known to contain reactive rock types. Consequently, because of the varied requirements, the geologist and project engineer should be aware of the reasons which justify use of a pozzolan in any given construction.

Conclusion

In the foregoing discussion the nature of pozzolans and their effect upon concrete have been stressed. However, in addition, economic factors may play a decisive role in selection of one satisfactory pozzolan or portland-pozzolan cement versus another, or in selection of a portland-pozzolan cement versus a portland cement, especially if technical factors, such as anticipated alkali-aggregate reaction or heat development in concrete, are not critical. Costs of purchase and transportation of the finished portland-pozzolan cement, or the purchase, excavation, haulage, processing, and blending of the pozzolan must enter into such cost analysis.

Current trends of thought anticipate that in a comparatively short time portland-pozzolan cement will displace use of straight portland cement in many situations. The accompanying demand for increased knowledge of the properties of pozzolan and for location of additional sources of materials presents a challenge to both the research laboratory and the engineering geologist.

SOME MINERAL AND FOSSIL COLLECTORS THOUGHTLESS

The Department has received complaints that some mineral and fossil collectors are seemingly without feelings of responsibility when making excavations on highway rights of way and on private property. Instances have been cited of places where literally tons of rocks and clay have been picked down and left in highway ditches, blocking drainage. This type of collecting will tend to give all collectors a bad name and ultimately place obstacles in the way of geological field work. Shovels should be carried on field trips and when group trips are made an official inspector should be selected from the membership to see that ditches are cleaned and all litter taken care of.

INVENTORY OF WASHINGTON NONMETALLICS

The Washington Division of Mines and Geology has recently published an inventory of Washington nonmetallic minerals as Bulletin 37. This bulletin, entitled "Inventory of Washington Minerals, Part I: Nonmetallic Minerals," is a 12 by 18-inch paper-bound, 113-page edition consisting of 30 maps and text. Each map shows the general distribution of a given nonmetallic resource in the State and also locates all known occurrences of that mineral in the State. The text opposite each map gives location, description, and value of every occurrence indicated on the map. The nonmetallic minerals are in alphabetical arrangement and the information is concise, complete, and easily readable.

Bulletin 37 is for sale by the Department of Conservation and Development, Olympia, Washington, for \$1.00

OREGON MARBLE QUARRY CHANGES HANDS

According to the Newsletter of the Raw Materials Survey, the Pacific Carbide and Alloys Company, Portland, has bought the property of Enterprise Lime Company from the Reconstruction Finance Corporation. The quarry and three kilns are located near Enterprise, Wallowa County. The limestone will be used in making calcium carbide at Portland.

NEW BOOK ON NORTHWEST IRON ORE DEPOSITS

"A Review of the Iron Bearing Deposits in Washington, Oregon, and Idaho" is the title of a bound volume just issued by the Raw Materials Survey, Portland. The author is Carl Zapffe, Manager of the Northern Pacific Railway Company's iron ore properties and a well-known authority on the iron ore industry. Mr. Zapffe has first-hand knowledge of the iron ore deposits of the Northwest and has had long experience in following the development of various projects for studying these ores along with plans for putting the deposits into production. The book shows an admirable balance between the practical and the theoretical in evaluating possibilities of utilizing such deposits. The Raw Materials Survey has a limited number of these books for sale at \$2.50.

NEW GOLD CONCENTRATOR

Production of a compact, lightweight, portable gravity concentrator has been announced by the Northwest Machine Works, Portland, Oregon. The machine, invented by Mastin Taylor of Helena, Montana, has a rated capacity of ten tons of minus quarter-inch per hour. The current model consists of a trommel, hopper, and two concentrating bowls 12 inches in diameter arranged in series. The production model of the machine, which is to be available on or about October 1, will be equipped with two 16-inch bowls. This unit will have a capacity of about 25 tons per hour and will weigh 600 pounds. The machine is reportedly designed so that it can be dismantled into several small units for transportation by airplane or mule back.

R.I.P.

The domestic mercury industry has about succumbed. Production of mercury in the second quarter of 1949 was at an annual rate smaller than in any year covered by the production record beginning with 1850 according to the U.S. Bureau of Mines in its Mercury Report No. 91. Primary production for the quarter amounted to 1,460 flasks or at an annual rate of 5,840 flasks. This compares with 51,929 flasks in 1943, the high point in domestic war production.

During the second quarter of 1949 the principal production came from the Bonanza mine, Douglas County, Oregon, and the Mt. Jackson (including the Great Eastern) mine, Sonoma County, California.

Imports during the quarter amounted to 29,492 flasks - a new high record for a 3-months' period. Italy, Mexico, Yugoslavia, Spain, and Japan supplied the metal imported, with Italy supplying 92 percent. Most of the imported metal was purchased by the Economic Cooperation Administration and was consigned to the national stockpile.

Domestic consumption was 7,600 flasks for the quarter. Although this figure is at a rate less than war and postwar rates, it compares favorably with the prewar rate of consumption.

The market price for the metal during the second quarter showed weakness and the average was \$6 a flask less than in the first quarter. A recent quotation in the E&MJ Metal and Mineral Markets gave the price as \$73-\$74 a flask.

EUGENE MEETING OF MINERALOGICAL SOCIETIES

The Northwest Federation of Mineralogical Societies held its 1949 convention in Eugene, Oregon, September 2, 3, and 4, under the sponsorship of the Eugene Mineral Association. Through the generous cooperation of the University of Oregon, exhibits and lectures were held in buildings on the campus. The principal speaker was Dr. Warren D. Smith, professor emeritus and former head of the University Department of Geology and Geography. Many fine exhibits were shown on the main floor of McArthur Court. At the annual banquet Mr. Phil Brogan of Bend, the well-known writer on Oregon geology, was master of ceremonies.

PERCENTAGE DEPLETION ALLOWED PERLITE AND DIATOMITE

Section 9 of H.R. 5268 which amends certain provisions of the Internal Revenue Code provides for percentage depletion of deposits of perlite and diatomaceous earth. Depletion allowance for these two minerals has not heretofore been allowed in the code. It is proposed to allow percentage depletion with respect to perlite and diatomaceous earth only in the dry crude mineral form before grinding or any other preparation for any particular market. As with other minerals in the group, 15 percent of the gross income is allowed and the provision makes inapplicable to these two minerals allowance of depletion on the basis of discovery value. The Senate Committee on Finance has reported favorably on the amendments and has recommended passage of the bill.

NORTHWEST NEEDS INDUSTRIAL CARBON

Industrial carbon, an essential material in the development of Northwest metallurgical industries, must be developed in large quantities or brought into the region economically if Northwest industrial expansion is to continue. This is the meat of a report just issued by the Department of the Interior Pacific Northwest Field Committee. The author is Ivan Bloch, consultant. Aluminum production in Washington and Oregon now requires about 160,000 tons of petroleum coke a year. Industrial consumption of coke and coke breeze is between 100,000 and 150,000 tons. Practically all of this carbon must now be shipped in. The report is entitled "Survey of Industrial Carbon Requirements of the Pacific Northwest" and is available at the Department of the Interior Pacific Northwest Field Committee, 506 Failing Building, Portland 4, Oregon.

DOMESTIC PRODUCTION OF ROOFING GRANULES IN 1948

According to U.S. Bureau of Mines Mineral Market Report No. 1755 Revised, production of roofing granules in the United States during 1948 was 1,485,690 tons valued at \$20,977,831, or an average per ton of \$14.12. The production in the various classifications was as follows:

<u>Classification</u>	<u>Short tons</u>	<u>Value</u>	<u>Average value per ton</u>
Natural	448,150	\$ 3,828,307	\$ 8.54
Artificially colored	1,002,430	16,563,351	16.52
Brick	35,110	586,173	16.70

MILL TAILINGS OWNERSHIP

Of considerable interest to mining men is the decision regarding ownership of mill tailings handed down in the Nevada Supreme Court recently. Briefly stated, mill tailings are personal property and are not subject to location as part of a mining claim. This holds true even for tailings from custom mills which treated ore belonging to one or more owners.

EXPLORATION UNDERWAY AT TUNGSTEN PROPERTY

Surface exploration work is continuing at the Bratcher tungsten mine near Ashland, Oregon. Present work is planned to determine the lateral extent of the ore as well as to explore the immediate area for additional deposits. Initial shipment of 97 tons of ore to the Tulare County tungsten mines plant at Lindsey, California, yielded 109 units of tungsten trioxide.

OREGON GOLD LODE PROPERTY INSTALLS MILL

Operations have begun at the Gold Plate mine near Galice, Josephine County. A four-stamp mill has been installed and milling is expected to begin in the near future. The mine is owned by W. W. Phillips and Charles Skeeters.

URANIUM DISCOVERY

A potentially important discovery of uranium bearing ore in the Marysvale, Utah, district appears to contradict all the accepted theories concerning secondary uranium deposits.

Heretofore the theory has been that secondary uranium ores do not occur over large areas and that they are not highly disseminated through the formations. Ordinarily (in this country at least) they appear in small lenses in sandstone (such as the carnotite in Colorado and Utah) or in narrow veins in granite formations. Neither do soluble secondary uranium ores usually persist to a depth of more than a few feet at the most.

But in the Marysvale discovery all these generally accepted rules are contradicted. A sulphur colored ore, which appears to be autunite, is widely disseminated in an andesitic porphyry which is bounded on the north and south by rhyolite porphyry. It has been drilled to a depth of 135 feet along a 30° slope for a distance of 800 feet along the slope and is several hundred feet in width.

Autunite is a calcium-uranium-phosphate which in the pure state contains 60 percent uranium oxide. It fluoresces brightly, as does the Marysvale ore. Small samples of the discovery have shown a uranium content of 0.36 to 0.76, which is within the range of shipping quality. Its high solubility indicates an easy milling problem and the size of the deposits, which might be much greater than explorations to date have shown, suggest that it could be mined by low-cost open pit methods.

The property is being developed by the Bullion Monarch Mining Company.

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