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STATE DEPARTMENT OF GEOLOGY AND MINERAL INDUSTRIES
Head Office: 702 Woodlark Building, Portland 5, Oregon

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QUICK-SETTING CEMENT FROM OREGON BAUXITE

Soon after the discovery of ferruginous bauxite in northwestern Oregon it was suggested by the Department that one possible use of the material was in making aluminous or quick-setting cements. Samples were submitted to cement companies for testing work along these lines. A few months ago Professor R. W. Moulton, Department of Chemical Engineering, University of Washington, informed the Department that early in 1948 a thesis had been written at the University of Washington giving results of testing work on northwest high-alumina clays and Oregon bauxite to indicate their possible application in making quick-setting cements. Subsequently Professor Moulton submitted a copy of the thesis with permission of the University and the authors to publish it. The essential parts of the thesis by Messrs. Arthur H. Every and George L. Hagen are reproduced herein. Some of the theoretical and experimental data have necessarily been condensed. It is believed that the thesis indicates a possible new use for Oregon bauxite.

Aluminous cement is made by only one manufacturer in the United States even though the product has found a wide use for special purposes. It would seem as if the peculiar properties of such cement would warrant a greatly expanded use if it were more readily available. An interesting feature of the testing work described by the thesis was the by-product of metallic iron. This feature especially warrants further research. The total amount of iron in Oregon bauxite may be reckoned in millions of tons. Titanium also is present in substantial amounts, and it would be desirable to find out how it acts in the cement-making process.

The Editor.

THE PRODUCTION OF ALUMINOUS CEMENT FROM NORTHWEST METERIALS*

By

Arthur H. Every and George L. Hagen

Status of Aluminous Cements

Physical properties of the cement

Aluminous cement, also variously called high-alumina, alumina, Lumnite, and Elektroschmelz cement, and Ciment Fondu, is not a new product, but has been known for a number of years. It was first introduced in France early in this century.

It is in the unique physical properties of concrete made from aluminous cement that the reason for its extensive use in Europe and specialized service in the United States is found. It is the only true very-rapid-hardening cement, and exhibits the strength within 24 hours which is reached by regular portland cement only after 28 days. Even the so-called high-early-strength portlands require 3 to 5 days to approach the aluminous 24-hour strength. The following table taken from data of Bates[1] gives a comparison between portland cement and aluminous cement as to strengths in pounds per square inch.

Table 1.

Strength of Portland and Aluminous Cements

	Portland psi**	Aluminous psi
1. Tensile - 1:3 mortar		
24 hours	122	372
28 days	383	425
2. Compressive - 1:3 mortar		
24 hours	475	5,615
28 days	2,650	5,835
3. Compressive - 1:2:4 concrete		
24 hours	---	2,880
28 days	2,410	2,845

The figures given in Table 1 are not to be considered as strictly representative of either cement, but were available values which Bates considered typical. It is interesting to note that the very marked superiority of aluminous cement is not so noticeable in the tensile strength. However, it has been found that the ratio of compressive to tensile strength in the latter is greater than in portlands, and for that reason, it is not practical to use the tensile test as a measure of the value of aluminous cements. This test is no longer specified by the United States Bureau of Standards for portland cement, either, for it is, of course, the compressive strength to which cements owe their constructional value.

Another important advantage of this cement over portlands, and actually the one which led to its development, is its resistance, unequalled by any other constructional cement, to chemical attack by sulfate and sea waters. Among its earliest uses was in railway tunnel construction in Southern France, where water containing considerable calcium sulfate had caused crumbling and cracking of the regular concrete work so seriously as to cause nearly complete collapse. However, after the installation of alumina concrete, this action was completely stopped, and this concrete is still good today. This concrete was also used in construction work on piers and piling at the Puget Sound Navy Yard at Bremerton, Washington, where sea water would be destructive to normal concrete.[2]

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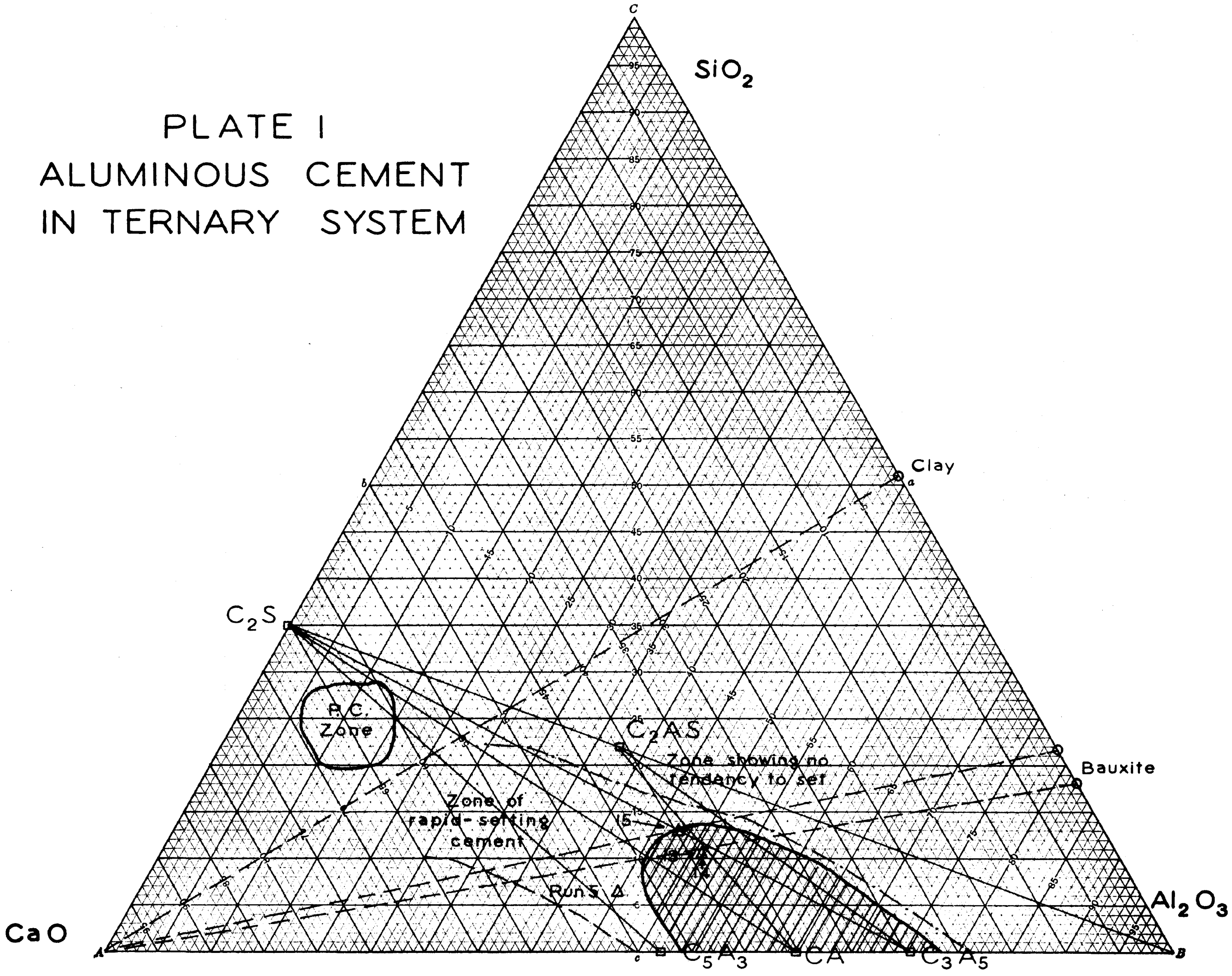
*Thesis submitted for the degree of Bachelor of Science in chemical engineering, University of Washington, 1948.

**Pounds per square inch.

[1] Bates, P.H., "High-alumina hydraulic cements": <u>Ind. and Eng. Chem.</u>, vol.18, pp.554-559, 1926.

[2] Bates, P.H., <u>Idem</u>.

PLATE I
ALUMINOUS CEMENT IN TERNARY SYSTEM



Because of its rapid hardening, the heat of hydration of alumina cement is more rapidly given off, allowing the concrete to be used at freezing temperatures which would normally damage portland concrete. Of course, this high heat has disadvantages, for higher temperatures, of approximately 145° F., hinder proper hardening and setting, and in addition, large masses of this concrete could not be poured because of the serious entrapment of too much heat. This latter difficulty has been overcome in some cases by constructing the main mass of a dam, pier, etc., of portland, then placing a relatively thin layer of aluminous cement about it, rendering the whole structure impervious to chemical attack. Aluminous concrete binds with portland concrete successfully.[3]

Other advantages claimed for the cement are: a favorable setting time, approximately the same as for portlands; absolute stability in volume; and stability in storage.

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[3] Lea, F. M., and Desch, C. H., The chemistry of cement and concrete, pp. 38-80, 290-320, London, Edward Arnold and Co., 1940.

Chemical properties of the cement

The chemical composition of this cement can be noted by a comparison with a typical portland cement.[4]

	Portland percent	Aluminous percent
SiO_2	22.0	5.0
Al_2O_3	6.5	42.0
Fe_2O_3	3.0	10.0
CaO	63.0	42.0

It can be seen that there is a large replacement of silica with alumina and subsequent lowering in the lime content. Thus the calcium silicates, principally tri- and di-calcium silicate, are replaced by calcium aluminates. These aluminates, as commonly written in the composite-oxide form, are calcium aluminate, $CaO \cdot Al_2O_3$ (abbreviated CA); tri-calcium penta-aluminate, $3CaO \cdot 5Al_2O_3$ (C_3A_5); penta-calcium tri-aluminate, $5CaO \cdot 3Al_2O_3$ (C_5A_3); and di-calcium aluminum silicate, $2CaO \cdot Al_2O_3 \cdot SiO_2$ (C_2AS). These compositions are located in Plate 1 (p.25) following the ternary diagram of the system. Because of the lack of clear information, iron has not been included, but is generally lumped with alumina in this diagram.[5] Tri-calcium aluminate, C_3A, gives a flash set on gauging with water and of course is avoided in the making of cement. C_5A_3 differs from the latter in showing no flash set, but nevertheless, the set occurs within 5-15 minutes, and owing to this rapidity, its actual value is doubtful. Both CA and C_3A_5 in the pure state rapidly attain high strengths and do not suffer from rapid setting. Bates[6] found final setting times of 2 and 8-16 hours respectively for these compounds. C_2AS seems to show no hydraulic properties. From these considerations, the notation of the alumina cement zone, shown in the diagram, seems valid.

The role of iron oxide in cement seems to be of minor importance, and the di-calcium ferrite formed does not contribute greatly to the strength.

The actual process of setting of aluminous cement is still a subject of some controversy, and the true mechanism is not completely agreed upon.[7]

Present manufacturing methods

In all present manufacturing processes, the raw materials are bauxite and lime or limestone. The method of manufacture is as yet far from standardized, and a variety of furnaces are in use. The most common production method is fusion in reverberatory open-hearth furnaces, arranged with a long vertical stack into which the bauxite and limestone are charged. It is fired with pulverized coal with a hot air blast. Fusion takes place at the point where the charge drops from the vertical stack into the furnace proper. The carbon dioxide and moisture are driven out the top, while the cement in the hearth is kept molten by heat radiated from the arch, and tapped out continuously from a tap hole. The temperature reached is about 1550-1600° C.

Electric furnaces have also been used at a number of plants in Europe. These are of the arc type, since the fused aluminates have too low a conductivity to allow the use of a resistance furnace.

All available references indicate that all commercial aluminous cements are completely fused, not merely clinkered as in the case of the usual portlands. Bates[8] states that alumina cements occur in a region where the temperature at which the compound is formed is considerably lower than in portland cement, and the compounds are also formed where slight changes in composition will require marked changes in the temperature needed to bring about

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[4] Bates, P. H., op. cit.

[5] Lea, F. M., and Desch, C. H., op. cit.

[6] Bates, P. H., op. cit.

[7] Lea, F. M., and Desch, C. H., op. cit.

[8] Bates, P. H., op. cit.

the desired reaction. Thus there is a narrow range where the mixture is a clinker of the desired composition, outside of which it is a mixture of unreacted raw material or a liquid. Some writers contend that complete fusion is absolutely necessary for good results. Hussey[9] states that complete fusion appears to have a very important bearing on other properties of the cement besides hydraulicity.

The rate of cooling is, according to Hussey,[10] an important variable in manufacture. Slow cooling is best, but the actual rates are based upon experience and are carefully guarded trade secrets.

The hard pigs of fused cement are crushed and ground to about the same size as portland cement, preferably within only 10 percent on a 150-mesh screen. The cement is very hard and causes considerable wear on the grinding equipment.

Raw Materials Used

The two principal raw materials used to make the cement were: (1) high-alumina clay obtained from Southwestern Washington deposits, and (2) ferruginous bauxite from deposits in Northwestern Oregon.

Castle-Rock clay

This was the first material tried and most of the work was done using it. This clay is of a group of transported and decomposed feldspars commonly called kaolin, or kaolinite, with the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. There are rather extensive deposits of these clays, varying somewhat as to composition, depth of overburden, etc., to be found in Southwestern Washington and Northwestern Oregon. The particular material that was used is known as Cowlitz or "Castle-Rock" clay, obtained from deposits near Castle Rock, Washington.

The analysis of this clay shows approximately this composition:

	Raw pct	Calcined pct
Al_2O_3	37.35	45.8
SiO_2	41.22	49.2
Fe_2O_3	4.13	5.0
Ignition loss	17.30	----

The material is located in Plate 1, the ternary phase diagram, on an iron oxide-free basis. It is immediately apparent from a glimpse of the tie-line that if only lime were added to this material the high-alumina zone located on the diagram would be missed, and no cement of the properties desired could be made, without the further addition of pure alumina, or chemical beneficiation. Such physical methods as flotation beneficiation would not solve the problem, for the silica impurity is tied up in molecular structure in the kaolin. An important factor, then, in the use of this raw material would be the ability to develop an economical enriching process. Since there has been considerable work done in an attempt to utilize these clays as a source of alumina production, the logical approach to this problem would seem to follow along these lines. However, the discouraging fact remains that if these would not be economically possible for the production of the relatively valuable aluminum, it is unlikely that they could be applied to this baser product. If, however, a process could be found that would give partial purification at a low cost, the answer might be found.

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[9] Hussey, A. V., "The applications of aluminous cement and its influence on concrete construction": Chem. and Ind., 1936, pp. 1037-1045.

[10] Hussey, A. V., Idem.

Ferruginous bauxite

The other raw material, given the name ferruginous bauxite, is of laterite origin, located in sizeable deposits in Northwestern Oregon, especially Columbia County.[11] Although the compositions vary with location, two different samples used by these investigators show the following analyses, the first material (with the lower silica content) is of the classification known as "upper pisolitic fine," while the second is a typical mining mix."

	(1) pct	(2) pct
Al_2O_3	34.20	34.20
Fe_2O_3	33.99	34.00
TiO_2	6.43	6.40
SiO_2	6.62	9.50
Ignition loss	18.71	15.90

Both of these samples were obtained from Alcoa Mining Company which is conducting experiments as to the uses of this material as an aluminum source. The samples of this bauxite are located on the ternary diagram, on an iron- and titanium-free basis.

The economic study of these deposits has not been so thoroughly investigated by the authors as the kaolin clays, but it seems probable that the bauxite deposits would provide a satisfactory source from the standpoint of cost of mining, available supply, etc.[12] The deposits average about fifteen feet in depth, with an overburden of 1½ to 30 feet, with the former figure the more common, mostly of silt.[13]

Experimental Work

Castle-Rock clay

The first experiments were performed with Castle-Rock clay to which technical grade lime was added to make up the calcium oxide content of the cement, while technical grade of alumina was used to bring the composition down nearer to the desired area of cements.

Fusion was first attempted in a small induction furnace. But this furnace failed to get up to the necessary heat for complete fusion. The authors then used a single-phase arc furnace for which they built a special graphite crucible in order to fuse small-run batches of cement.* The results of the runs on the clay as well as those obtained later on the bauxite are tabulated in Table 2.

After a number of unsuccessful runs, it was decided that experimentation further with the clay as a raw material would be useless, because of the amount of pure alumina that had to be added. For instance, the makeup of Run no. 6 was: clay - 370 grams, pure alumina - 550 grams, and lime - 645 grams. It can be seen that very little use was made of the clay, and the alumina would naturally be too costly as a raw material. In addition, it is to be remembered that the silica and alumina are tied together in the clay in a molecular structure and it is very probable that more rigorous conditions would be required to break these bonds and make the cement molecules.

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[11] Kelly, J. V., "High alumina-iron laterite deposits, Columbia County, Oregon": U.S. Bur. Mines Rept. Inv. 4081, 1947.

[12] Libbey, F. W., Lowry, W. D., and Mason, R. S., "Ferruginous bauxite deposits in northwestern Oregon": Economic Geology, vol. 41, no.3, pp. 246-265, 1946.

[13] Kelly, J. V., op. cit.

* The original thesis fully describes the performance of the furnace and the behavior of the clay during experimentation.

Table 2.

Tabulation of Experimental Results

Run number	Raw material	Composition of feed				Strength psi		Comments
		Al_2O_3 pct	CaO pct	SiO_2 pct	Fe_2O_3* pct	24 hours	7 days	
1	Clay	40.0	40.0	10.0	10.0	----	----	Incomplete fusion
2	Clay	44.5	44.5	11.0	----	----	----	Incomplete fusion
3	Clay	44.5	49.0	6.5	----	----	----	Good fusion, hydraulic
4	Clay	46.7	40.8	10.4	2.1	----	----	Incomplete fusion, no hydraulic properties
5	Clay	44.0	49.0	6.5	0.6	----	----	Good fusion, flash set
6	Clay	47.0	43.0	10.0	----	1,949	3,592	Fusion, 2 hours
7	Pure components	47.0	39.0	8.0	6.0	1,320	1,870	Fusion, 3 hours, Fe_2Si formed
8	Clay	47.0	43.0	10.0	----	1,636	1,623	Incomplete fusion, 2 hours
9	Bauxite and clay	37.6	34.1	8.0	20.0	----	----	Easily fused, 2 hours
10	Bauxite and clay	45.0	37.0	8.0	10.0	244	1,640	Clinkered
11	Bauxite and clay	45.0	37.0	8.0	10.0	1,076	1,500	Nearly complete fusion, 2½ hours
12	Bauxite and clay	45.0	37.0	8.0	10.0	----	----	Electrode fused into charge, no results
13	Bauxite	25.0	40.0	5.0	30.0	4,350	6,100	Good fusion, Fe reduced, 1 hr., 45 mins.
14	Bauxite	25.0	40.0	5.0	30.0	3,030	6,060	Good fusion, 1 hr., 30 mins.
15	Bauxite	24.2	40.0	6.8	28.7	4,270	5,810	Good fusion, 1 hr., 30 mins., autoclave- 0.08 pct expansion

*Includes TiO_2.

Ferruginous bauxite

Further experimentation, then, was conducted with the furnace and other equipment using the bauxite from the Oregon deposits. The first really indicative results were made on Run no. 13, which had the following analysis, both as predicted by the composition and amounts of raw materials added, and by actual determination, as previously described:

	Predicted pct	Actual pct
Al_2O_3	25.20	39.65
CaO	40.40	39.30
SiO_2	4.86	11.10
Fe_2O_3	29.70	9.95

The feed was 1000 grams calcined bauxite plus 675 grams CaO.

The strengths obtained with the compression cubes were:

	psi
24 hours	4,350
7 days	6,100

These strengths compare favorably with most commercial aluminous cements, and greatly surpass the strengths attained by portlands for these same periods of time.

It will be noticed that the iron content is considerably below that predicted, and that, comparatively, the alumina and silica contents are higher. The reason for this is the reduction of much of the iron. A single button of iron of 250 grams from a 1,675-gram charge was taken out, and there were other small pieces imbedded in the graphite crucible. The presence of so much iron oxide in the raw material was a problem because of its deleterious effect on the cement, and this reduction thus easily solved the problem of removal of much of it and gave very good strength characteristics to the product. The reduction took place of course on the bottom and sides of the graphite crucible. Because this cement showed promise, an autoclave expansion test, in which a pressure of steam of 295 psi is maintained for about three hours on the formed neat-cement mold, was conducted. This was to determine the expansion of the cement under severe conditions, and this sample showed only 0.08 percent expansion, which is well under the allowable value of 0.5 percent. Gillmore time-of-set tests were made, and they showed about 1 hour 15 minutes for initial and 5 hours 30 minutes final set. These values compare favorably with portland cements and are within the limits specified by the Bureau of Standards.

In order to determine roughly for certain if it was iron that was reduced and not such a substance as ferrosilicon, tests were made of the pig. These volumetric titrations showed about 98 percent iron, so it was definitely established that this was iron. No attempt was made to find a complete metallurgical analysis for such substances as arsenic, phosphorous, etc.

To determine the reproducibility of this cement, two more runs were made of the same starting composition. The strengths obtained with these products were:

	No. 14	No. 15
	psi	psi
24 hours	3,030	4,270
7 days	6,060	5,810

For Run no. 14, the 24-hour strength is lower than the earlier run, but the reason for this mainly lies in a faulty preparation of one set of cubes, for in tamping them, insufficient pressure was used, and there were air spaces, or honeycombs which definitely lowered the 24-hour strength. Not all of the cubes were in this condition, and on the 7-day test, only two of the three were counted because the third was honeycombed and showed much less strength. This would not, of course, be considered as a strictly reliable procedure, but for the comparative purposes of this work, it was believed to be justifiable. Run no. 15 also compared favorably with no. 13.

It is quite possible, of course, that these runs would not be strictly reproducible in commercial practice, for the reduction, being dependent upon the graphite of the crucible and electrode, would vary with the rate of feed, time of fusion, arc tension, current, and many other variables which were impossible to keep constant with the setup used. However, the fact that their characteristics were so similar indicated that they would probably be representative of the commercial product.

Conclusions

1. Castle-Rock clay is not suitable for the manufacture of aluminous cement because of its high silica content.

2. If Castle-Rock clay is used for cement, it would have to be beneficiated. It is doubtful if the cost of beneficiation would warrant its use in cement.

3. It is more advisable to utilize ferruginous bauxite from this same general locality.

4. Experimantal work indicates that despite its high iron content, a suitable mixture of the ferruginous bauxite and lime or limestone will produce a good aluminous cement.

5. The value of the iron formed in the process is uncertain since a complete metallurgical analysis was not performed. It is possible that a commercial grade of iron could be obtained.

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OLD MINE REACTIVATED

According to Mr. E. R. Waite of Waite Minerals, Inc., Grants Pass, the lower tunnel of the Cowboy copper property, Waldo Mining District, southern Josephine County, is being extended with the objective of cutting the ore exposed in the winze 200 feet above. Eight men, two shifts a day, are presently employed, Mr. Waite stated.

The Cowboy has a record of production estimated at $300,000, and although the property has been known since about 1900, most of the production was in the period 1928-1930. Values have been mainly copper and some gold.

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ADMINISTRATION BACKS SYNTHETIC FUEL BILL

John R. Steelman, assistant to the President and acting chairman of the National Security Resources Board, has written the House and Senate Interstate and Foreign Commerce Committees that he is in favor of legislations to accomplish the purposes of the Synthetic Fuels Bill. This bill includes $400,000 to reimburse the Alabama Power Co. for large-scale underground gasification experiments to determine whether coal in place can be burned and whether resulting gases are suitable for synthetic fuel purposes.

From Compact Comments published by Interstate Oil Compact Commission, Oklahoma City, Oklahoma, April 1, 1949.

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UNITED STATES GOLD AND SILVER MOVEMENTS IN FEBRUARY 1949

The monetary gold stock of the United States was increased during February by $18,429,000 to $24,289,635,000 at the end of the month as the combined result of earmarking operations, receipts from foreign countries, exports, domestic production, and other factors. Gold held under earmark at the Federal Reserve Banks increased during February by $22,200,758 to $3,802,549,285.

Gold exports in February totaled $4,499,082 and imports $25,978,267. Silver exports totaled $260,861 and imports $3,278,067. Principal gold exports were to Greece, $2,026,972 and Danzig $1,575,003. Principal imports were from Union of South Africa, $21,128,599. Principal exports of silver were to United Kingdom, $120,580 and principal imports from Mexico, $1,727,947.

From World Trade News published by Field Service, United States Department of Commerce, March 31, 1949.

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NEW MEMBER DEPARTMENT GOVERNING BOARD

Mr. Mason Bingham, Portland, has been appointed by Governor Douglas McKay as a member of the Governing Board of the State Department of Geology and Mineral Industries. Mr. Bingham succeeds Mr. E. B. MacNaughton who had expressed a desire to be relieved of his duties as a member of the Board at the expiration of his term on March 16. The State Senate confirmed Mr. Bingham's appointment on April 2. His appointment is for a 4-year term beginning April 4, 1949, and ending March 16, 1953.

Mr. Bingham has been prominent in Oregon business circles for many years. He is manager of the Lewis Investment Company, which owns the Benton Mine, the largest producing gold mine in southern Oregon until it shut down because of war conditions. He is chairman of the Multnomah County Tax Supervisory and Conservation Commission as well as being a director in the First National Bank and the M. & M. Woodworking Company.

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NEW BULLETIN WITH GEOLOGIC MAP ISSUED

The geology of the Kerby quadrangle, located in southwestern Josephine and southeastern Curry counties, is the subject of a bulletin including a colored geologic map, which has just been issued by the State Department of Geology and Mineral Industries. This bulletin was prepared and published as a cooperative project between the Department and the U. S. Geological Survey.

Authors of the bulletin are Dr. Francis G. Wells, who was in general charge of the field work, Preston E. Hotz, and Fred W. Cater, all geologists with the Survey.

The field work covering the bulletin and map started in 1940, suspended during the war period, resumed in 1945, and was finished in 1947. Besides the areal geology a total of 188 mines and prospects are shown on the map which covers an area of nearly 75 square miles. Much of this area is rough and inaccessible. Some of the towns and place names in the quadrangle were important in the early boom days nearly 100 years ago. Known deposits of copper, chromite, and gold are scattered throughout the quadrangle area.

The bulletin, Number 40, is entitled Preliminary Description of the Geology of the Kerby Quadrangle, Oregon, includes the geologic quadrangle map in the pocket, and may be obtained at the Portland office of the Department in the Woodlark Building, Portland, Oregon, or at the field offices in Baker and Grants Pass. Price postpaid is 85 cents.

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GOLD

According to an item in the "Mining World" of London, England, C. J. Turle, chairman of Hampton Gold Mining Areas, Ltd., is completing a special report on the world gold price in relation to the economic future of the English speaking nations. The report, when completed, will be sent to President Truman and U.S. Treasury officials. In the meanwhile, the group of gold producers, which Mr. Turle represents, has cabled President Truman recommending a high world gold price.

Congressman D. A. Reed (R-N.Y.) has introduced bill H. R. 3262 into Congress, to allow a free circulation of gold, redemption of paper money for gold, to establish and maintain a domestic gold coin standard, and for the repeal of the Gold Reserve Act of 1934. The bill does not call for any increase in price of gold or silver.

One of our prominent business magazines, in commenting on the sale of South African gold above $35.00 per ounce, states that the latter price is becoming "shaky," and the International Money Fund is badly worried about it. The magazine indicates the $35 price is too low.

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According to reliable newspaper advices, gold is selling in Manila at $44.00 to $47.50 an ounce, and in 1948 the Mysore Mine in India sold its entire production at 21 pounds sterling an ounce, the equivalent of $84.00 in U. S. money.

From News Letter, published by Mining Association of Montana, Butte, April 1949.

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