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The commercial preparation of baryta

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REPORT

OF THE

ORIGINAL INVESTIGATION

IN THE SUBJECT:

"THE COMMERCIAL PREPARATION OF BARYTA."

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THE COMMERCIAL PREPARATION OF BARYTA.

The object of this investigation was to ascertain in a general way the methods employed at the present time in mining, milling and leaching baryta, and the commercial uses to which the product is put, with the idea in view of improving these methods and encouraging a more extended use of the product if possible.

Casual reading of the statistical reports had impressed us with the fact that either an enormous expense was involved in preparing the product as used in commerce or an immense financial profit was being reaped by the mill men.

The Government reports show that Missouri produces more than 50% of the total output of baryta, with Tennessee, Virginia, South Carolina and Kentucky, in the ordernamed, as the other producers.

Personal investigation has developed the information that, while at present in Missouri, Washington County is producing practically all the marketed baryta, a number of other counties have extensive deposits of the mineral and in our opinion present even better fields for operation than does Washington county. There are, however, difficulties connected with the handling of the material from these deposits which will necessitate some changes in the present methods of dressing and these difficulties have engaged out thought and attention to a considerable extent in this investigation.

Baryta, ($BaSO_4$), also spelled barite and barytes, is a crude form of barium sulphate and is usually associated with clayey oxides of iron, zinc, lead and other ores. In some cases of vein occurrence it forms the matrix or gangue matter of lead sulphide but insuch quantities not sufficient to pay for mining. In general, it occurs in rough, disturbed areas in irregular form and usually quite near the surface, seldom being mined at greater depth than fifteen feet.

Geologists are in doubt as to the movement of this mineral, the question being a wholly undecided one and will not be discussed here. It is sufficient to say that it is practically insoluble in any liquid, even the strongest acids and alkalies attacking it but slightly.

The mineral has a specific gravity of about 4.6; hardness of 3; is crystalline, of pearly lustre, brittle and decrepitates at comparatively high heat.

As found in nature baryta has various shades and colors, from pearly white to opaque, dark brown, depending upon the impurities associated, but when clean after washing and bleaching is a perfect white. The most usual color is yellowish-white , the color being given to it by associated iron oxides.

The chief use of baryta is in the manufacture of pigments, more than 80% of the total production being used in this purpose. Paper manufacturers use it in certain qualities of paper to give weight and body. Meat packers use considerable quanitites in making the canvas covers of cured meats impervious to air, insects, etc. It is generally thought also to be used as an adulterant of sugar, candy and various food stuffs, but our investigation has failed to develop information showing such uses.

The use of baryta in pigments originally was an adulterant, but experience has proved that it has a useful value in itself and is extensively used by the best paint manufacturers in combination with zinc white and white lead as a consitituent of the paint body. In fact pure baryta in oil is on the market in competition with lead and zinc pigments. It seems to have somewhat less covering power per volume, but by weight is quite equal to that of lead and is a permanent color; not being affected chemically by gases or the weather.

Besides the uses given above, baryta is used a s a blast furnace or converter flux for the reduction of lead and other ores. This use of the mineral, however, is liminted to small quantities and then only in regions where it can be had very cheaply.

Our investiggation has developed no additional possible uses for the mineral in sulphate form, though we suspect many cou ld be found by going more deeply into the subject from an industrial standpoint. But the use of other compounds of barium is extensive, and strange to say, that while America produces large quantities of baryta , with many known fields still undeveloped, there is practically not a pound of these compounds manufactured from our native mineral, all being imported from Germany. The field for a manufacturing chemist in this line appears to be a good one as there is no reason why all such compounds cannot be made in America from American baryta.

The following table shows the production and value of crude baryta for 1903 in the United States. This value is for the crude mineral at the mills.

The price for the floated mineral varies between eight and eighteen dollars per ton, while that of the Blanc Fix or precipitated barium sulpahte averages thirty dollars per ton.

Production of Crude Baryta in the United States in 1903.

State	Ton quantity	Value
Missouri	23178	$ 77712.00
North Carolina	6835	21347.00
Tennessee	14684	32691.00
Virginia	5700	20400.00
	50397	$152150.00

Besides the domestic product ion of the crude mineral as shown by the above table, there was imported in the same year from foreigh countries, 5716 tons of manufactured baryta, valued at $48726.00, and 7105 tons of crude baryta, valued at $22777.00. The inports are increasing each year for the reason that onaccount of the weight of the mineral and its cheapness in foreign countries it makes excellent ballast for transports returning unloaded.

The statistics for 1904, 5 and 6 will surely show a great increase in the production of baryta in the United States especially in Missouri and a corresponding increase in imports.

From the above data the value of the industry is shown to be of no inconsiderable amount, being a total of $152150.00 to the miners and something like four time that amount to the manufacturers of baryta in the United States, while the total valuation of the imported product is $71503.00 . To these totals must be added $224539.00,- being the value of the imported compounds of barium, a large percentage of which is manufactured from the mined baryta giving a grand total of $448292.00.

The names and locations of the plants producing manufactured baryta in the United States are as follows;-

The Point Mining and Milling Co., Mineral Point, Missouri.;

Nulsen, Klein & Krausse Mfg. Co., St. Louis, Mo.;

J.C. Finck Mineral Milling Co., St. Louis, Mo.,;

Bristol Baryta Mills, Bristol, Tenn.;

Commercial Mining and Milling Co., Knoxville, Tenn.;

Nulsen, Klein and Krausse, Lynchburg, Va.;

Clinch Valley Barytes Co., Honaker, Va.;

Pittsburg Baryta and Milling Corporation, Richlands, Va.;

The largest producer is the Nulsen, Klein & Krausse Mfg. Co., of St. Louis, Mo. Five of the above mills started in 1903 and for a time lowered the price by over-production. Three of the mills are down at the present time.

The field of baryta in the sections now producing in Missouri seems to be inexhaustable, but difficulty is experienced in securing sufficient quantities for full mill capacities. This is probably to be accounted for by the low price paid the miners, and somewhat by the crude methods of mining. The latter is simply a hand gouging process, no mining machinery being used at all.

The average price received by the miner per ton of mineral mined is $2.25, which means, at the ordinary rate, about $1.00 per day for his labor.

The undeveloped fields of baryta in Missouri are in Cole and Miller counties, where the mineral occurs in larger deposits(sometimes in fairly well defined leads) associated with blende crystals and occasional crystals of Galena.

It is to the problem of separating the latter minerals from the baryta that our interest is due in selecting this subject for special investigation. The nearness of specific gravity values of Blende and baryta, being 4.1 and 4.5 respectively, prevents an hydraulic separation, and because of no known process of economic separation these excellent fields have remained idle of investigation and development.

Our first idea was that a separation might be effected by a decrepitation and screening method. Both these minerals decrepitate, but it was thought that the temperature causing same for each mineral would be sufficiently far apart to allow of the process. Our experiment proved that while blende decrepitated to a thorough fineness at a comparatively low temperature, the baryta also decrepitated at the same temperature to such an extent that screening would be impossible. We are still of the opinion, however, that some method of separation exists for these minerals and are at present working on one involving the idea of "Flotation". A satisfactory research in this direction is impossible at this time, but will be continued in the future.

So at present the hand-picking, crushing and leaching method remains the only practical one and following will be found a complete description of this method in detail as used by the Point Mining and Milling Company of Mineral Point, Mo. In our opinion, the details there used could be changed to considerable advantage in designing a new mill, and in reviewing the process we have indicated some of the proposed improvements.

As a matter of fact, the designers of this mill, Messrs. Macklin and Stroop, have, by working along trained technical lines created a vast improvement over the old process and much credit is due them for their presistent determination to succeed in producing a single, uniform product each day from any grade of raw material. This they are doing daily with a demand for their product greater than they can supply.

Their process is as follows;- (See diagram next page for flow sheet.)

Scales

Bins

12" Crusher

Elevator

Bin

Inclined spiral screw washers

Inclined spiral screw washers

Inclined spiral screw washers

Washed baryta | Slimes and dirt → To waste

Wheeled to floor near slip mill

Slip Mill

Centrifugal Pump

12 Hydraulic Classifiers

Float Stuff | Oversize → To Slip Mill

Settling Tanks

Sludge to Leaching Tanks | Water siphoned Off

Sulphuric Acid Added&
agitated by steam from
bottom.

To Pump Tank

To Lead Cast Pump

To Washers # 1,2 &3.

Settling Tanks

Sludge which is leached white
to hopper of sludge dryer | Water siphoned off

Sludge Dryer
Spiral Conveyor & Elevator
Pulverizer
Sacking & Weighing Machines
Stock Bins.

The ore as received at the mill is either hauled in from the surrounding country or is shipped from nearby stations and will run probably 97 to 99% $BaSO_4$, the impurities being Fe_2O_3 and some SiO_2, Ca and Sr. In some cases the Fe_2O_3 is nearly all as scale and has to be chipped off. Again it more or less stains the whole piece and occasionally they get what the miners call " resin spar", which has a brownish color throughout the whole piece and is very hard to leach. The silica is there as dirt or in cavities.

The bins are on the same level as the crusher jaws and will hold about five hundred tons. The ore is hand fed to the crusher, which is an old style, 12" Blake type and is set to 1". The ore crushes very easily and the percentage of fines runs quite high. It is then elevated to a bin and fed to a series of three inclined spiral washers,- the inclination of which is some 15 degrees,- the discharge of one being the charge of the other. Here the dirt and some fine baryte is washed out and goes to waste. The last one discharges onto the floor and is wheeled from here in barrows to the slip mill.

There are two slip mills each able to handle from fifteen to eighteen tons in twenty-four hours. The mills are a mechanical development of the old Arastra idea. The sliding stones are so fixed that additional bearing power can be put on them thus increasing their capacity. The mill is also arranged with an auxillary steam cylinder which operates the long end of a lever; its use being to raise the work ing parts in order to make repairs or replace machinery or stone parts.

The only ore that can get out of this mill is such that can float through a trough the bottom of which is about 9" below the top of cir-cular inclosure to the mill. This sludge is raised by means of a centrifugal pump to a multiple arrangement of hydraulic classifiers.

There is one baffle plate extending some 18" into the water and the overflow is of very slight velocity and about 1/8" deep.

It is from this part of the process that the baryta receives its name of "float" baryta. The heavier material that does not float over settles to the bottom and is drawn off and returns to the slip mill by gravity.

The overflow goes to a series arrangement of four settling tanks, there being two series of four connected in multiple. A tank after filling is shut off from the rest and allowed to settle for fifteen minutes and then the water is drawn off by a siphon and used again for milling purposes.

The sludge is taken from the bottom of the tank through an opening to the leaching tanks which are lead lined. The sludge contains some 10 to 15 % of water as moisture and to this is added 100 to 150 # of 50 % commercial sulphuric acid per ton of mineral treated. Steam is admitted at the bottom of the leaching tank and the whole mass thoroughly agitated for eight to twelve hours depending upon the amount of impurities. Near the end of the process samples are taken from time to time and the color compared with a standard color.

This hot mixture is drawn off to a lead lined tank and kept agitated. The tank acts as a suction for a lead cast pump which raises it to a series of washing tanks, three in number.

These tanks are arranged in steps, the top of each succeeding one being some three of four feet lower. They are cylindrical with a diameter of about ten feet and extend downward some ten feet and terminate in an inverted cone of height about six feet.

The mixture is fed on to a stationery round inclined table and there met by a stream of filtered water. Inside the tanks is placed a hollow cylinder which is large enough to leave a margin around the edge between it and the circumference of the washing tank of about one foot. This hollow cylinder extends down inside until it nearly reaches the cone part of the tank. From the table it is fed through little troughs into this outside compartment; the heavy barite settles to the bottom and on the inside of the cylinder the clear acid water rises to an overflow which conveys it to waste. The difference of specific gravity of the masson the the outside of the hollow cylinder and the clear liquid within is very preceptible being showh by a difference of level of some six inches.

The discharge of this first tank goes to the second. The mixture was too heavy to siphon well so a small stream of water is admitted to the siphon pipe just below the tank, this water being under pressure carries the mixture to the next tank. Each succeeding tank is analogous to the first one.

There is no danger of spoiling or discoloring the product in the first two tanks but in the third one extreme care has to be used. If all the acid is removed the mineral takes on a brownish discoloration which hurts it commercially; if too much acid is left in, it cannot be shipped in bags and it lowers the grade and price. The end point is determined by means of Potassium Cyanide showing a blue discoloration. This is not so much an acid test as it is an indicator of the presence of ferrous and ferric salts. If the product is washed too much the ferric salt has a tendency to re-precipitate giving the discoloration mentioned above. Thepotassium cyanide shows by the blue discoloration when all the ferrous salts have been removed.

The sludge is drawn off from here to a series of four settling tanks and the water siphoned off and used for mill purposes. When ready to be dried it is agitated by means of revolving paddles and enters the hopper of the sludge drier. It is kept agitated here and fed through a large number of small pipes onto an inclined plate which feeds the sludge regularly to the revolving drum by means of impact. The sludge falls onto this drum, which is heated internally by steam, and in one revolution it is dry, and just before reaching the feed point is scraped off and falls into a spiral conveyor. As it is likely to dry in lumps it is taken through a pulverizer by means of an elevator, the pulverizer is run at the rate of 3000R. P. M, and then discharged through a chute to be sacked and weighed.

In washing out the acid it is very essential that the water be thoroughly filtered. For this purpose they have a series of some six large cast iron tanks partially filled with crushed granite which seems to do the work admirably, By changing the connections and reversing the direction of water flow, the filters can be cleaned in a few moments.

In reviewing the process, the replacement of the slip mills with French pebble mills, which can be used on either wet or dry material, would more than double the capacity without increasing the labor of feeding the crusher, for one man could easily feed through 35 to 50 tons in ten hours. We would put the mineral through the same kind of washing arrangement and have the product elevated to a self feeder for the pebble mills.

With the slip mill arrangement now in use, i f a device for feeding, having the feed immediately precede and revolve with the stones, could be installed, the capacity could undoubtedly be increased some 20 to 25 percent.

They have some fifteen small leaching tanks and it would undoubtedly be a saving to have a fewer number of larger ones.

Say that the process was similar from here on to the discharge of the leaching tanks; here draw off as done now and allow to settle and then siphon off the hot sulphuric acis with the salts it might contain to evaporating pans and concentrate the solution by heating,- then allow it to cool and thus precipitate the bulk of the salts. The acid could then be mixed with new acid and used again, even though it did contain iron salts.

We titrated some of the liquid before washing and it showed that from 50 to 60 % of the acid had not been used.

Then dilute the sludge which had settled to the bottom of the tank with filtered water and agitate, and if convenient have the mixture go by gravity to the washing tanks. It would require less washing which could probably be done for the present capacity with two instead of three tanks.

The balance of the process carry out as they have it.