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BENEFICIATION OF A ZINC RICH OXIDIZED ORE FROM
NUEVO LEON, MEXICO.

BY
JORGE CASAS NIETO.

A

THESIS

submitted to the Faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1947

Approved by

A. Legsdin

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Beneficiation of a zinc rich oxidized ore from Nuevo León,
México.

by J. C. Nieto.

INTRODUCTION

Rich zinc ores are relatively rare now in this country but are still abundant in countries like México, that have not yet developed all their mineral potentialities. In almost all Mexican zinc districts there has been reported sporadic production of oxidized ores, although until now no specially designed plants have been built for the beneficiation of such ores. Generally the zinc carbonate and zinc silicate ores are hand picked and shipped to this country for beneficiation. The Mexican production of zinc ores has never been steady, because of economic factors such as bad transportation systems and lack of market for the product. The following table⁽¹⁾ shows typical production figures by States.

(1) Secretaría de Industria, Comercio y Trabajo. Departamento de Minas. México. Anuario de Estadística Minera. vol. 14, p. 622; vol. 15, p. 645; vol. 16, p. 592; vol. 17, p. 580.

Table I.-Mexican production of oxidized zinc ores, in short tons.

State	1928	1929	1930	1931
Chihuahua	---	50	---	---
Coahuila	32287	23183	260	50
Guerrero	---	20	30	92
Hidalgo	28	---	---	---
Jalisco	1799	611	272	100
Nuevo León	275	2109	---	---
San Luis Potosí	---	45	---	---
Tamaulipas	127	---	14	---
Zacatecas	1637	2746	205	---
Undetermined	---	---	153	---
Total	36153	28845	934	242

During the last few years, particularly after the outbreak of the second World War, there has been in México an increasing demand for zinc oxide to be used in the rubber and paint industries. This product has to meet rigid specifications, similar to those established by the Bureau of Standards of this country⁽²⁾. These permit 1.0% maximum of plus 325 mesh particles, and 98% minimum of ZnO, when this product is obtained by the "American Process"; that is, when it is produced directly from the ore, without producing first zinc metal. In view of this, the actual processes for the production of zinc oxide from oxidized ores require at least two stages: first, the production of a "dust" that must

(2) U.S. Bureau of Standards, Circular No. 87, 1920. Standard Specification No. 3, p. 2.

assay between 60 and 70% Zn, and, second, the refining of this product for the preparation of purified zinc oxide. It is the first step, that of beneficiating a zinc ore that assays about 40% Zn, that has been studied as a research problem. Even below this grade an oxidized zinc ore can be treated successfully by pyrometallurgical methods for the production of zinc oxide. The actual market conditions specify a minimum of 40% Zn for the buying of raw ore; Zn content below 40% is penalized.

Zinc oxide has been utilized in numerous industries because of a white color and covering power, as well as some other properties. The most recent data on the application of zinc oxide in this country, are shown in the next table:⁽³⁾

Table II.-Distribution of zinc oxide sales in U.S.A., 1939-1943, by Industries, in short tons.

Industry	1939	1940	1941	1942	1943
Rubber	70187	70979	90429	52717	67898
Paints	25334	23268	30304	25122	29852
Chemical warfare	---	---	---	---	21801
Floor coverings and Textiles	5641	4752	6991	5224	6633
Ceramics	6572	6352	8596	2934	3203
Other	<u>6818</u>	<u>7862</u>	<u>12513</u>	<u>13680</u>	<u>14015</u>
Total	114552	113213	148833	99677	143402

(3) U.S. Bureau of Mines, Minerals Yearbook, 1943, p. 212

SCOPE OF WORK DONE

The beneficiation of zinc ores for the production of zinc oxide is most properly carried out in the so called Waelz kiln. But such an installation, even for experimental purposes, is quite expensive and requires a long time for the complete set-up. On the other hand, the metallurgical reactions accomplished in this process are very simple because they depend only on the volatilization of the zinc formed by the decomposition of zinc ores. Because of the above reasons, it was decided to carry out volatilization tests in a pot heated with gas and coke, collecting the fume produced in a small flannel bag. These tests showed the amenability of this particular ore for the Waelz process.

Some concentration tests were also run in an attempt to improve the grade of this ore. Only the flotation process showed an effective concentration, but the recovery was so low as to make this process impractical.

GENERAL DATA

The Dulces Nombres mine is located in the southern part of the State of Nuevo León, México. The distance between the mine and the nearest railroad station, measured on an all-weather road, is 44 miles. This railway station is known as Estación Adelaida on the Tampico-Monterrey main line and it is almost due east from the mine. The elevation of Estación Adelaida above sea level is 600 feet and the elevation of the mine is 7200 feet above sea level.

The deposit has been worked intermittently for lead and

zinc oxidized ores, exporting the raw material produced to this country. The company that owns the mine, "Plomo y Zinc, S.A.", has been producing during the last few years, about 100 tons per day of lead carbonates, that assay from 25 to 45% Pb, 2 to 5% Zn, and 15 oz. per ton of silver. As a result of past mining, this company has actually in stock piles about 8000 metric tons of oxidized zinc ore, and the underground developments show an additional 17000 metric tons of blocked out ore of the same kind. Thus, the existence of 25000 metric tons of oxidized zinc ore is quite certain. Different estimates of the probable ore have placed it at 75000 metric tons.

The geology of this type of ore is relatively simple. They are generally described in the literature as "replacement" deposits, when, like in this case, the country rock is constituted of "mantos" of limestones. Lindgren⁽⁴⁾ has explained the genesis of these deposits by assuming that the original zinc sulphide, sphalerite, is attacked by solutions rich in ferric sulphate, with the production of zinc sulphate, ferrous sulphate and sulphuric acid; the two latter substances promote the reaction again, attacking the ever present limonite. The zinc sulphate reacts easily with calcium carbonate of the country rock, and the zinc carbonate is produced. Because of the high solubility of zinc in ore deposits, the zinc solutions may penetrate deeply and it is not uncommon to find in this type of orebodies, secondary zinc shoots below the primary ore. In the case of zinc-lead combination, lead remains in its original place, as galena or cerussite, and zinc carbonate

(4) W. Lindgren. Mineral Deposits, 1934. pp. 851-852.

is found lower down.

As a consequence of its genesis, the exploitation of these deposits must be governed by certain general rules, such as the ones given by Bateman,⁽⁵⁾ according to which, the irregularity of the deposits in depth and grade must be taken into account before any metallurgical process can be designed. In this case, for instance, where only as little as 100 000 tons may be assured, it is not advisable to install any metallurgical plant with a capacity higher than 40 tons per day, because it is considered uneconomical to erect such a plant for a working period of less than ten years.

The zinc minerals in the Dulces Nombres ore are smithsonite, $ZnCO_3$, and hemimorphite, Zn_2SiO_4 , the first one being predominant. Iron oxide, as limonite, appears surrounding the zinc carbonate particles as a very thin film, and also as filling in the pore spaces. Some calcite is also present.

The chemical analysis of this ore is given in the following table:

Table III.-Chemical analysis of the Dulces Nombres ore, in %.

Zn	Fe	Pb	SiO_2	Al_2O_3
40.1	11.9	1.2	18.7	0.2

(5) A.M.Bateman. Economic Mineral Deposits, 1942. p. 272

BENEFICIATION BY ORE DRESSING METHODS

From the viewpoint of gravity concentration methods, the following specific gravities show that it is not possible to obtain any practical concentration of this ore.

Cerussite	Sp. Grav. 6.46-6.57
Hemimorphite	4.0 -4.2
Limonite	3.6 -4.0
Smithsonite	4.3 -4.45

In effect, the gravity separation of two minerals is governed by the criterion given by the formula:

$$\frac{d_1 - d}{d_2 - d} \cdot$$

where d_1 and d_2 represent the specific gravities of the heavy and of the light minerals, respectively, and d stands for the specific gravity of the medium in which the separation takes place. When the above ratio gives a figure higher than 1.5, the separation may be carried out efficiently; but if the value of that ratio is very small, the separation of two minerals by gravity concentration is impossible for all practical purposes.

In our case, the separation of smithsonite from limonite, the value of the above ratio is of the order of 1.2, too low to assure any efficient separation. Confirmation of the above statement was obtained by running two tests by tabling and jigging, on a sample ground to -20 mesh. No satisfactory result was obtained; it was observed that the concentrate was highly contaminated by iron oxide due to the intimate

mixing of the zinc carbonate and the iron oxide particles. Grinding to finer sizes produced so much iron slimes, that it was not considered worth while to run more gravity concentration tests.

The flotation process was tried along lines proposed by F. Bunge,⁽⁶⁾ using the same reagents. The procedure followed was such that it could be duplicated in actual practice. The successive operations were as follows: 300 grams of the ore were ground to -100 mesh in a pebble mill in 5 minute stages, to avoid overgrinding; desliming by decantation to remove the -400 mesh particles; agitation in a one liter flotation cell with the following reagents, each one added consecutively in 5 minute periods: 1.0 pound/ton of NaOH, 1.0 pound/ton of sodium silicate (N brand), 2.0 pounds/ton of citric acid; flotation with 0.8 pound/ton of sodium oleate, in the same flotation cell. The concentrate was cleaned twice without the addition of any reagent, and the final results are shown in the next table:

Table IV.-Flotation test results.

Product	Weight, %	Analysis, in %			Recovery, in % Zn
		Zn	Fe	Ins.	
Concentrate	18.9	37.0	4.3	13.6	17.6
Middlings	17.8	37.0	5.3	17.8	16.6
Tailings	63.3	41.2	17.4	20.2	65.8
Composite	100.0	39.6	12.7	18.5	100.0

(6) F. Bunge, Flotation of the oxidized ores of zinc. Thesis, 1946, Missouri School of Mines and Metallurgy, Rolla, Mo.

The above results show a poor recovery of the zinc and a good depressing action for the Fe, with the particular amount of reagents used. In view of this, it was decided to run another test that differed from the above one in the conditioning with sodium silicate and in the amount of sodium oleate used. The grinding, desliming and agitation operations, were the same as in the above test; the amount of sodium oleate used was 3.2 pounds/ton and the concentrate was cleaned four times. The middlings of this flotation were then mixed with the tailings and re-conditioned again with 3.0 pounds/ton of sodium silicate for 5 minutes; the pulp was deslimed and floated again with 0.8 pound/ton of sodium oleate, cleaning twice the concentrate obtained. This concentrate is called Concentrate 2 in the next Table, that shows the final results obtained:

Table V.-Flotation test results.

Product	Weight, %	Analysis, in %			Recovery, in % Zn
		Zn	Fe	Ins.	
Concentrate	21.2	44.4	8.2	13.8	23.7
Concentrate 2	18.8	40.6	16.0	17.4	21.6
Middlings	24.8	39.4	14.0	20.4	24.6
Tailings	35.2	35.0	7.9	19.8	30.1
Composite	100.0	39.7	11.0	18.2	100.0

The purpose of the above test was to obtain separate concentrates of the smithsonite and of the hemimorphite (Concentrate 2); but the results of Table V, though indicating some concentration, do not show a clean separation of

the zinc minerals, and, moreover, the attempt to float a big amount of zinc minerals resulted in high contamination with iron. As the tailings were still very high in Zn, the process was considered unsuccessful and no more concentration tests were run.

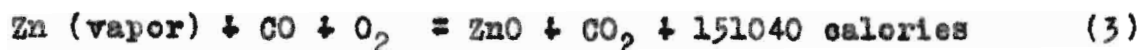
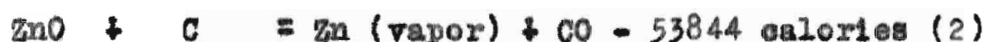
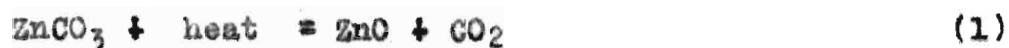
BENEFICIATION BY VOLATILIZATION

The high content in Zn of the Dulces Nombres ore led to the assumption that the most adequate procedure for the beneficiation of this ore would consist in some form of volatilization, resulting in the production of zinc oxide. A review of the literature on this subject showed that the Waelz process can accomplish this beneficiation economically, even for ores the zinc content of which is much lower than the ore studied here. It was decided, then, to run volatilization tests that would prove or disprove the applicability of the Waelz process for this ore.

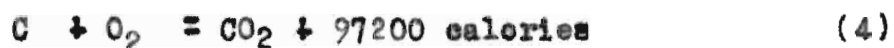
By "volatilization" is meant here, a metallurgical process that consists essentially of two steps: the first one, is the group of physico-chemical processes that decompose the ore and produce a zinc rich product; the second one is the mechanical action of removal of this product by means of some gaseous stream or current. It is on this basis that the Waelz process works effectively for the beneficiation of zinc, lead and tin ores. O. Barth,⁽⁷⁾ has given a very complete description of the fundamentals and operation of

(7) O. Barth. Die Metallverfluchtungsverfahren mit besonderer Berücksichtigung der Herstellung von Zinkoxyd, 1935. Wilhelm Knapp. p. 117-147.

the Waelz process, and, according to him, the reactions that successively take place in a Waelz kiln, are as follows:



The addition of the last two equations gives:



It must be noted that the reaction (1) starts at 137 degrees C and ends at 440 degrees C,⁽⁸⁾ and takes place in the solid charge itself inside the kiln. The reaction (2) has an equilibrium temperature of 911 degrees C at 760 mm. of Hg, and also takes place inside the charge. On the other hand, the reaction (3) takes place on the surface of the particles that constitute the charge, and the presence of an excess of oxygen decreases the partial pressure of the carbon dioxide.

Thus, the volatilization of zinc does not need any heat at all, and the heat supplied in the industrial process will be, theoretically, only that necessary for the decomposition of the zinc carbonate and will be supplied by the combustion of the fuel used. It so happens that secondary reactions, such as the expelling of moisture and decomposition of silicates, or physical conditions, such as heat radiation or absorption by a big surface, make it necessary to supply heat in order to keep the temperature of the charge inside the Waelz kiln at about 1100-1200 degrees C.

As it is generally described, a Waelz furnace is nothing but a rotary cylindrical kiln, with a slope of about 4%,

(8) O. Barth. op. cit. p. 48.

where the charge is fed at the upper end and goes downward by a slow rotary motion of the order of one revolution per minute. The mineral, generally ground to $\frac{1}{8}$ inch, is mixed with coal or coke so that the fuel in the charge constitutes about 20% of it. Gas is supplied, either in counter-current or in parallel current system, inside the kiln, and the fume product is collected, after cooling and precipitation, in bag houses in which there are facilities for packing and shipping of the final product. Temperatures inside the charge are very difficult to measure, but the outlet gases are generally at 500-600 degrees C; this value corresponds to a temperature inside the charge of the order of 1100-1200 degrees C. The graph below, taken from Barth,⁽⁹⁾ shows the range of temperatures inside the Waelz kiln, when working in counter-current, as well as the length of the preheating and dezinking-

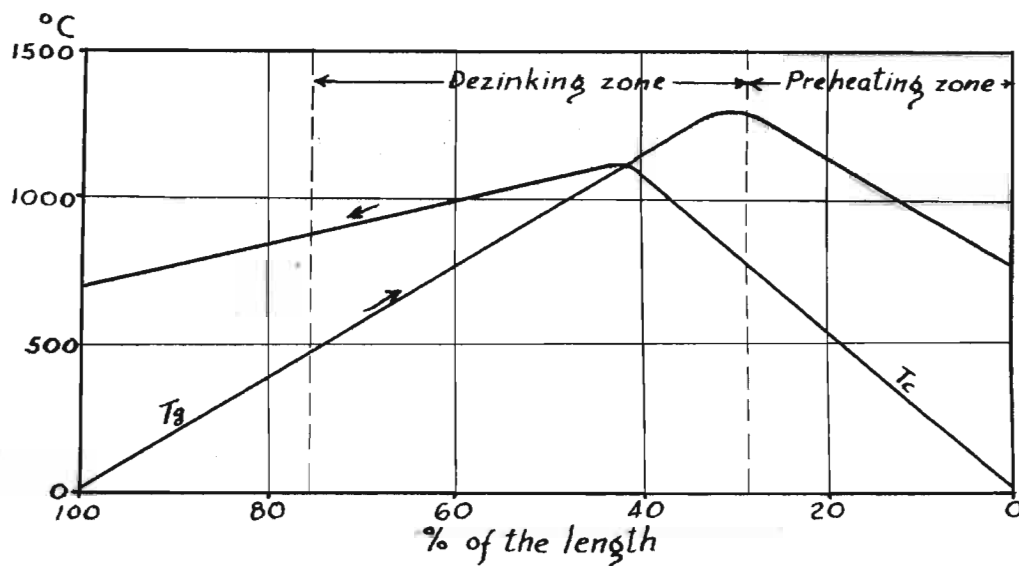


Fig.1.-Temperatures in a Waelz kiln, working in counter-current. T_c =Temperature of the charge. T_g =Temperature of the gas.

(9) O. Barth, op. cit. p. 126.

ing zones.

The two great advantages of the Waelz process, are: first, it is a continuous process, and second, it permits a close control of the temperature by regulating the amount of gas admitted inside the kiln. The first advantage arises from the rotary motion of this furnace, and the second one requires generally that the kiln should be worked in counter-current system. These advantages make it possible to treat by this process almost any kind of zinc ore, and successful operation has been reported on ores that assay as low as 6% Zn. On the other hand, the operation of this furnace gives trouble because of the formation of incrustations on the lining, that require complicated operations to remove them and that limit the length of the kiln to about 120 feet when the inside diameter is of the order of six feet.

The volatilization tests were carried in a cast iron pot, 6½" inside diameter and 8½" height, with an iron grid in the bottom, that was introduced into another pot, 9" high and 8½" inside diameter. The exterior pot was provided with a flue, 36'-9" length and 2" diameter, at the end of which was placed a wool bag. A water manometer was connected to the flue at 5" from the exterior pot, and a thermometer was placed at 34" from the second pot. A mixture of air and gas was fed into the pot from the top, and the downward suction was provided by means of a 2" blower, at 20' from the exterior pot. Figure 2 shows a sketch, not drawn to scale, of this apparatus.

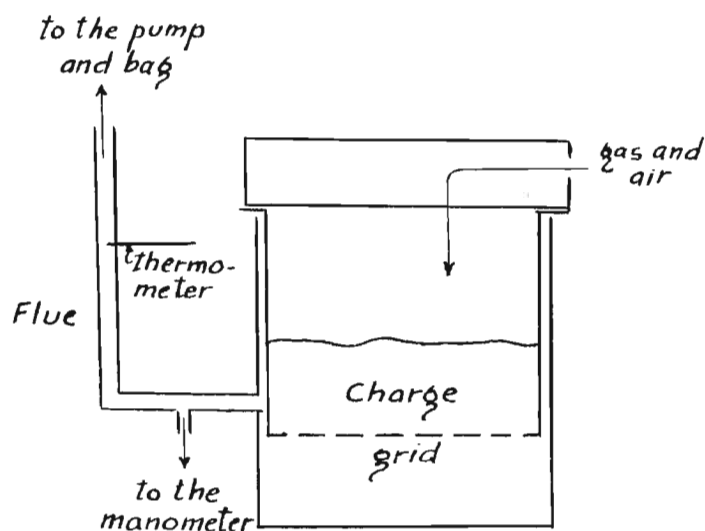


Fig. 2.-Sketch of the volatilization pot.

The charge consisted of a mixture of ore and coke, both of them ground to minus 1/8 inch. The coke used had 5.0% moisture and 10.4% ash, the ash being 73.0% insoluble and 16.5% Fe. In all the tests the amount of coke was kept constant at 30% of the total charge, this figure being in excess of that used in Waelz kiln operations. In order to simulate the conditions of the Waelz process, stirring of the charge was provided manually by means of an iron rod. The maximum temperature that could be read on the thermometer at the position indicated, was 540 degrees C, this figure corresponding to about 1200 degrees C in the pot itself. The tests were run for periods of one to two hours at constant temperature. It was necessary in all cases, to spend about one hour in slowly raising the temperature. Chemical analysis of the residues and of the bag dust were run for all tests, the flue

dust being impossible to collect, because of the adherence of the oxide particles to the walls of the flue.

A number of tests were run, the last one indicating a recovery of about 70% of the zinc in the charge, and giving a product assaying 62% Zn. The results of five tests are indicated in the next tables, showing how the conditions of temperature, vacuum, and stirring, affected the results. As the purpose of these tests was not to reproduce actual plant operations, but to show the amenability of this ore to volatilization, no additional tests were carried out.

Table VI.-Volatilization test No. 1

Time: one hour.

Temperature: 460 degrees C at the thermometer.

Charge: 1400 gm. of ore.

600 gm. of coke.

Manometer: 10".

No stirring.

Products	Weight, gm.	Analysis, in %				Distribution,	
		Zn	Fe	Pb	C	Ins.	% Zn
Residue	1795	24.3	8.8	--	21.5	12.9	75.1
Bag dust	38	29.6	2.1	25.0	2.1	2.2	2.0
Flue							22.9
Feed	2000	28.1	8.3	0.8	25.4	15.5	100.0

The results of this test were completely unsatisfactory. Lack of stirring caused definite channelling of the gas stream, leaving a great part of the charge practically undecomposed. So, for the second test, manual stirring was provided, as indicated above, by means of an iron rod.

Table VII.-Volatilization test No. 2

Time: one hour.

Temperature: 460 degrees C at the thermometer.

Charge: 1400 gm. of ore.

600 gm. of coke.

Manometer: 10".

Stirring every ten minutes.

Products	Weight, gm.	Analysis, in %					Distribution, % Zn
		Zn	Fe	Pb	C	Ins.	
Residue	1600	20.8	9.7	--	20.9	11.4	59.2
Bag dust	46	40.3	0.7	19.3	3.2	3.0	3.3
Flue							37.5
Feed	2000	28.1	8.3	0.8	25.4	15.5	100.0

Stirring of the charge materially improved the grade of the product, as compared to the first test, and decreased the zinc content of the residue. It was thought that the time had not been enough to complete the reactions, and in the subsequent tests it was increased to two hours to obtain a bigger output. According to Harris,⁽¹⁰⁾ this is the average time that it takes the charge to go through a Waelz kiln of regular size.

(10) W. E. Harris, The Waelz process. Transactions of the A. I. M. E., vol. 121, 1936. p. 707.

Table VIII.-Volatilization test No. 3

Time: two hours.

Temperature: 460 degrees C at the thermometer.

Charge: 1400 gm. of ore.

600 gm. of coke.

Manometer: 9".

Stirring every ten minutes.

Products	Weight, gm.	Analysis, in %				Distribution,	
		Zn	Fe	Pb	C	Ins.	% Zn
Residue	1460	20.8	8.1	--	21.9	14.0	54.0
Bag dust	65	46.4	2.7	18.4	9.9	2.8	5.4
Flue							40.6
Feed	2000	28.1	8.3	0.8	25.4	15.5	100.0

The increase in time did not give a much better recovery, though it permitted the collection of more dust of better grade than in the above tests. The next variable to be changed was the vacuum as recorded by the water manometer, in an attempt to produce more pure zinc oxide by a separation of the lead and zinc oxides. It is true that some Waelz installations produce leaded zinc oxide, but this requires a close control of the charge composition and of the temperature. Although this condition might be tried for the Dulces Nombres ore, its success would be very doubtful because of the fact that the orebodies contain either lead carbonate ore of high grade, 35% Pb, or zinc oxidized ore of about 40% Zn. On the other hand, the Waelz process is perfectly applicable for the production of lead oxide from lead carbonate ores. The principles of lead volatilization, are, of course, the same as in

the case of zinc.

Table IX.-Volatilization test No. 4

Time: two hours.

Temperature: 460 degrees C at the thermometer.

Charge: 1400 gm. of ore.

600 gm. of coke.

Manometer: 3".

Stirring every ten minutes.

Products	Weight, gm.	Analysis, in %				Distribution,	
		Zn	Fe	Pb	C	Ins.	% Zn
Residue	1540	14.8	8.5	--	23.8	15.8	40.2
Bag dust	68	50.9	2.8	16.9	9.6	2.8	6.2
Flue							53.6
Feed	2000	28.1	8.3	0.8	25.4	15.5	100.0

The decrease in vacuum improved somewhat the zinc grade of the product, but it did not do very much for the separation of lead and zinc oxides. In view of this, the only way to effect this separation was by a modification of the bag itself. The sketch below shows the bag used for

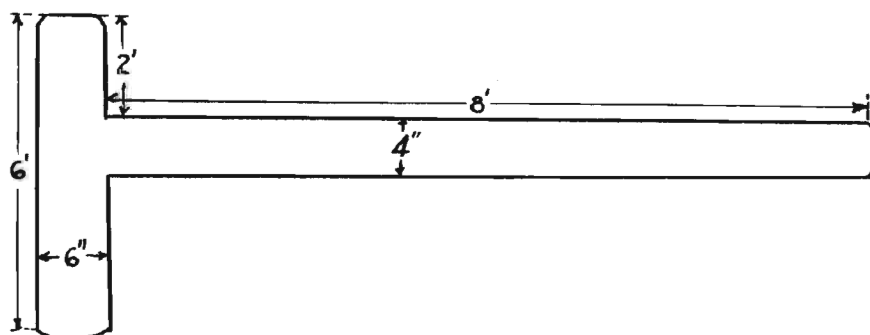


Fig. 3.-Bag used for the separation of Pb and Zn oxides.

the last test; the vertical portion was supposed to keep a great deal of the lead oxide and the horizontal part was designed to catch a purer zinc oxide. An increased temperature and faster stirring also had influence on the results of Table X, corresponding to the last test.

Table X.-Volatilization test No. 5

Time: two hours.

Temperature: 540 degrees C at the thermometer.

Charge: 1400 gm. of ore.

600 gm. of coke.

Manometer: 2-3".

Stirring every five minutes.

Products	Weight, gm.	Analysis, in %				Ins.	Distribution, % Zn
		Zn	Fe	Pb	C		
Residue	1385	11.6	15.4	--	19.2	11.4	28.6
Bag dust 1	101	35.5	4.0	14.1	4.6	3.8	6.4
Bag dust 2	70	62.3	2.4	5.8	3.2	0.4	7.8
Flue							57.2
Feed	2000	28.1	8.3	0.8	25.4	15.5	100.0

The results of the last test were satisfactory enough for the purpose of this work: to show that this ore may be volatilized for the production of the so called "technical" zinc oxide. It must be noted that in all the above tests the flue content could not be collected, because of the type of apparatus, but in actual operations, the flue dust is, of course, recovered very easily. That these tests indicate the applicability of the Waelz process for this ore is shown by the fact that the metallurgical reactions are the same for

both cases; decomposition of the zinc minerals, reduction of the zinc oxide to zinc vapor, oxidation of the zinc vapor to zinc oxide, and transport of this oxide by means of a gaseous current, to a collecting bag. The condition of temperature is also the same on both cases; between 500 and 600 degrees C for the outlet gases. Stirring of the charge and the flowing of a gas current, simulate the same phenomena of the Waelz kiln. It may be mentioned in this respect, that the U.S. Bureau of Mines has recently applied a similar experimental procedure to show the applicability of the Waelz process for volatilization of Mexican tin ores.⁽¹¹⁾

(11). W.G.Sandell, L.C.Bauerle and K.C.Bean. U.S.Bureau of Mines, Report of Investigations No. 4080, June 1941.

CONCLUSIONS

A zinc rich oxidized ore from the state of Nuevo León, México, has been examined for its beneficiation. Due to its high content in zinc, concentration by ore dressing methods is not considered as an economically important problem. However, various tests were run on gravity concentration and flotation methods. Both processes showed negative results, due mainly to the particular arrangement of the zinc mineral particles and the iron oxide particles. Some volatilization tests indicated the amenability of this ore for the Waelz process. A "technical" zinc oxide was produced in these tests, by means of a volatilization pot, simulating in the best possible way, the metallurgical conditions of a Waelz kiln. The final product assayed about 62% Zn, 2% Fe and 6% Pb. Further refining of this product is necessary for the production of commercial zinc oxide.

In view of the above results, the economics of the exploitation of the Dulces Nombres ore, may be governed by the next two conditions:

1)-The high content in zinc permits direct sale of the raw ore to United States plants that are producing zinc oxide. 40% Zn is the lower limit for the acceptance of such ores without penalty.

2)-Installation of a Waelz Plant at the nearest place to the mine where metallurgical facilities may be available for the production of zinc oxide and subsequent sale of this product either in México or in this country. As was noted before, such an installation should not be planned.

until the existence of oxidized ores in sufficient amount for a working period of the plant of, at least, ten years has been proved. The smallest unit of this type reported in the literature for the treatment of zinc ores, has 5' inside diameter and 98' length. According to Barth,⁽¹²⁾ the capacity of a Waelz kiln may be figured on the basis of one metric ton per 24 hours per cubic meter of space inside the kiln. So, the unit mentioned above may treat 53 metric tons of ore per day, and for continuous working during ten years, assuming 300 working days per year, it needs 159000 tons of ore. As this figure is much higher than the ore actually proved, the installation of a Waelz unit should be preceded by more development work in the Dulces Nombres mine, or in some other mines of the northern states of México, where oxidized zinc ores have been produced in the past.

(12) O. Barth, *op. cit.* p. 134.

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