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The Effect of Certain Minerals
upon
The Volatilization of Silver Chloride

7836

Boyd Dudley, Jr.

The work undertaken in this investigation was first suggested in connection with the analytical determination of Silver and Chlorine by weighing silver chloride. Later, however, the experiments assumed a metallurgical character.

The final purpose of the experiments was to determine the effect of a few of the common mineral constituents of ores on the loss of silver during a chloridizing roast. In the metallurgy of silver it is frequently necessary to change the silver bearing minerals into silver chloride.

This is done by roasting the ore in a furnace in the presence of salt. The salt is decomposed by certain constituents of the ore, and the silver is converted to silver chloride. The ore is then leached or amalgamated to remove the silver. In this roast a high loss of silver by volatilization is not uncommon. Causes of this volatilization are not well understood; so the problem under discussion is to determine the effect of the more common minerals upon this loss.

Attempts were not made to duplicate practical conditions; and the results obtained point in no way to the approximate loss of silver that might be expected, if the ores were chloridized on a large scale.

It is a common practice among students and laboratory experimenters to roast a small quantity of silver ore in a muffle, under chloridizing conditions. The loss of silver is then determined by assay of the original and roasted ore. Such a procedure gives no information as to the loss that might occur if the ore were roasted in a furnace on a commercial scale. It simply shows the loss in silver suffered by this particular ore under these particular conditions. This is true because conditions in the muffle are entirely different from those in the commercial roasting furnace. The more important of the factors governing the loss of silver are temperature, draft, time, stirring, and thickness of the ore bed. It may be readily seen that, with the possible exception of temperature, the conditions in a muffle are very different from those in a furnace. In the experiments performed the temperature was the only variable factor. All others were maintained as nearly constant as possible.

A brief description of the procedure followed in the experimental work will now be given:

Ten ores were prepared containing three minerals in varying proportions. The minerals were pure Silica, Calcite, and Pyrite. They were combined in the proportions shown by the following table:

Ore Number	Silica	Calcite	Pyrite
1	100	---	---
2	---	100	---
3	25	75	---
4	50	50	---
5	75	25	---
6	--	---	100
7	50	---	50
8	--	50	50
9	35	35	30
10	25	25	50

The minerals used were as pure as could be obtained. Each was prepared by grinding in stages and screening the whole pulp through a 40 mesh sieve.

Ten grams of each ore was carefully mixed with an amount of silver chloride containing 100 milligrams of silver. The mixture was then roasted in a three inch scorifier for one hour. A number of roasts were made on each ore at varying temperatures, and the loss of silver subsequently determined by a fire assay. In this way it was expected that enough data could be secured to plot a curve for each ore, showing the percentage loss in silver at varying temperatures. This expectation was not realized. In only one case is the data sufficiently consistent to plot an approximately general curve. This is with ore number three, and will be shown later. The results, however, taken as a whole, are consistent enough to point out several facts not mentioned in technical

books on the chloridizing roast.

The preparation of the Silver Chloride offered a difficulty, which at first appeared almost unsurmountable, but which was overcome in a rather simple manner. The silver chloride was precipitated from a filtered silver nitrate solution by an excess of hydrochloric acid. The precipitate was thoroughly washed, drained of as much water as possible, and preserved in a salt mouth bottle.

The bottle was painted black outside to exclude the light, which would reduce the silver salt. The open bottle and silver chloride were then placed in an air bath and dried for several days at 120 degrees C. On removal from the air bath attempts were made to pulverize the silver chloride in an agate mortar. Instead of breaking into a powder the salt simply packed down into a hard horny flexible mass, not unlike the mineral horn silver.

It appeared that experiments involving an intimate mixture of Silver chloride with gangue minerals were at an end. As was before stated, however, a simple and effective solution of the problem was discovered. Among druggists it is a known fact that gum camphor and other organic gums cannot be pulverized under ordinary conditions; but, if a few drops of alcohol are placed on the lump of gum, it may be readily reduced to powder. It appears that the alcohol or alcohol vapor so changes the particles of gum that they temporarily loose their cohesive powers. The liquid alcohol is also solvent for all such gums.

Reasoning from this, there seemed a possibility that some

reagents might have a similar effect upon the horny lumps of silver chloride.

Something might be found which would so alter the crystal faces of the silver salt that the small crystals would no longer persist in adhering so tightly together.

Naturally ammonium hydroxide was first to suggest itself. It occupies a position, with reference to silver chloride, analogous to that occupied by alcohol with regard to the organic gums. It is a good solvent for the salt, and the ammonia volatilizes very readily.

Small portions of the silver chloride were tried with relatively large amounts of concentrated ammonium hydroxide. Under these conditions the silver chloride was most easily reduced to the finest powder. Other portions of the salt were powdered with decreasing amounts of ammonia solution. Finally it was found that the silver chloride did not have to be wet at all. In fact six drops of concentrated ammonia solution will render one hundred grams of silver chloride easily pulverized.

The solvent action of the ammonia solution is apparently not essential. The ammonia gas is evidently the active agent. No experiments, however, were performed with the dry ammonia. If, after pulverizing, the ammonia is removed from the silver chloride by heating, the salt cannot be pulverized further; but resists all such attempts by becoming compact and horny again. For this reason it was determined to use a minimum amount (about six drops to 100 grams silver chloride) of the ammonia solution, and allow it to remain with the silver chloride. This was admissible, because

six drops of the solution weighs only about 0.2 gram, which in 100 grams will amount to only 0.2 %.

The preparation of the ores for roasting was as follows:

Ten grams of the mixed pulp was weighed. Then 163.8 milligrams of silver chloride, corresponding to 100 milligrams of Silver, was weighed on an Ainsworth gold balance. The silver chloride was transferred to an agate mortar, moistened slightly with ammonia solution and ground. The ore pulp was then placed in the mortar and, after carefully triturating for five minutes, the mixture was transferred to a three inch scorifier.

The roasting was performed in a Case muffle gasoline furnace with muffle 16 by 10 inches. Fifteen roasts could be made in this muffle at one time and a very constant regulation of temperature was secured.

The measurement of temperatures presented a rather difficult problem. At the time these experiments were carried out there was only one Platinum-Rhodium thermo junction in school. Since there were four other series of experiments in progress at the same time, in which temperature measurements were essential; this junction was overworked.

It was finally decided to construct a Copper-Nickel junction. This was done by fusing (in a blast lamp flame) one end of a copper wire six feet long to the end of a Nickel wire of the same length and diameter. The wires were long enough to reach from muffle to galvanometer, and no copper lead wires were necessary. The free ends were connected directly to a Weston direct reading millivoltmeter.

The wires were insulated from each other by inserting the Nickel wire into a porcelain tube, and drawing it through until only about two inches of the hot junction end protruded.

The copper wire was bound to the outside of the tube by means of loops of copper wire wound around the tube. The tube was about thirty inches in length, and served as a handle for the junction. The wires from tube to galvanometer were insulated by winding each with asbestos card.

The copper nickel junction gives a much higher potential at the galvanometer poles than does the Platinum-rhodium junction. Hence the millivoltmeter is sufficiently sensitive to measure the temperature to any desired degree of accuracy.

The instrument was calibrated by comparison with the Platinum-rhodium junction. This was done by placing the two junctions at the same point on the floor of a hot muffle. The deflection of each galvanometer was noted. A number of these readings were taken through a range of temperature, and from the data obtained, a deflection-temperature curve was plotted for the copper-nickel junction. The Platinum-rhodium junction had been previously calibrated by noting the deflections produced at the temperature of boiling water, boiling sulphur, boiling naphthalene, freezing aluminum, freezing silver and freezing copper.

To check the accuracy of this comparison calibration the copper-nickel junction was tested at the temperature of boiling sulphur and freezing aluminum. Since these two points gave results consistent with the curve, it was assumed that the calibration was correct.

In the use of copper nickel junction there are two difficulties. The more unimportant is, that the E.M.F. is slow to respond to changes in temperature at the hot junction. This is probably explained by the fact that the copper wire is a very good conductor of heat. When a change in temperature occurs at the junction, the conduction of heat to or from this point tends to bring the temperature of the whole length of the copper wire to the temperature of the hottest point, which is usually the junction. In this way the junction point ~~X~~ does not reach the temperature of surrounding objects until a considerable part of the copper wire has received heat from, or given heat to the junction.

A far more important disadvantage is, that after continued heating at high temperature the nickel wire becomes very brittle, and may break with even the most careful handling. This difficulty was overcome to a great extent by making a number of copper nickel junctions by fusing together wires about four inches longer than the porcelain tube, mentioned above. The asbestos covered lead wires were cut from the original junction. Then the short junction wires were connected by passing the nickel wire through the tube, and the copper wire through the loops outside of the tube. The junction wires were connected with their respective leads, and the junction was ready for use. This change could be made in five minutes, whenever the nickel ^{wire} failed. Care was taken to see that the total length of wire from junction to galvanometer was the same as when calibrated. All splices were carefully scraped and wound to insure good connection. In this manner the junction at a given temperature will, of course, deliver the same potential to the galvanometer poles as did the original junction upon which

the calibration was performed.

The roasts were kept in the furnace for one hour at a constant temperature. Alternate stirrings and temperature measurements were made during the whole time. A constant temperature was maintained by regulation of the pressure and amount of gasoline going to the burner. In every case the temperature measurements were taken by placing the junction on the surface of the roasting ore. This point was selected rather than the muffle floor, because the actual temperature of the roast depended largely upon the amount of pyrite present in the ore; while the muffle floor temperatures are practically the same at all points equally distant from the door.

In the early part of the work attempts were made to determine silver, and at the same time chlorine, in the roasted products by a wet method of analysis. All such attempts were finally given up on account of the fact that no exact and, at the same time, rapid method of analysis could be devised. Obviously the roasted silver chloride (if it remained in the ore as such) could not be completely extracted by any of the common solvents, as ammonium hydroxide, potassium cyanide, "Hyposulphide", etc. On account of this fact it appeared that any process of getting the silver into solution must be preceded by reduction of the silver chloride to silver, and removal of the chlorine.

Various attempts were made along this line. The ore pulp was mixed to a thick paste with dilute sulphuric acid and zinc dust. Powdered aluminium and the zinc copper couple were also tried.

If complete reduction can be secured the problem is solved. The pulp can be diluted with water, filtered and washed. The filtrate will contain all of the chlorine as hydrochloric acid. The residue contains the reduced silver and excess zinc dust. These metals may be dissolved in nitric acid, and the silver titrated with a standard solution of ammonium thiocyanate, using a ferric salt indicator. Chlorine may be determined in the filtrate by precipitation with an excess of a standard silver nitrate solution; following this by removal of the silver chloride, and a back titration of the excess silver with ammonium thiocyanate.

Weighed amounts of silver chloride were mixed with ore and treated as described. No consistent results were obtained. The analyses showed a reduction of from 50 to 90%, and even after standing twenty-four hours the reduction was never complete.

The wet determination of silver and chlorine was finally given up, and the fire assay for silver adopted. The scorification process was found to give the most satisfactory results. The roasted ore weighed about eight grams, hence could not be fluxed in a single scorification^{er}. Each portion was roughly divided into two parts, and each part was fluxed in a three inch scorifier. In all cases forty grams of test lead were used with the necessary amount of borax. With the ore^S containing high lime five to seven grams of borax glass was used. In the case of the silica and highly silicious ores two and one half grams of soda was used, giving a very clear fluid slag.

Lead buttons obtained from the scorifications were cupelled at feathering temperature and the resulting silver was weighed.

The following is a table of results, showing the percentage loss of silver sustained by the various ores.

The ores are referred to by number, and for the convenience the table showing their composition is again given here.

Ore Number	% Silica	% Calcite	% Pyrite.
1	100	---	---
2	---	100	---
3	25	75	---
4	50	50	---
5	75	25	---
6	---	---	100
7	50	---	50
8	---	50	50
9	35	35	30
10	25	25	50

Table of Results.

Ore No.	Temp. C	Loss of Silver
1	1000	92.7
1	800	85.5
1	715	79.1
1	700	77.1
1	660	72.7
1	385	13.2
1	340	8.2
1	310	12.4

Ore no.	Temp.C.	% Loss of Silver
1	255	9.0
1	250	8.2
2	975	94.2
2	975	96.5
2	800	95.4
2	750	92.3
2	700	78.2
2	535	39.7
2	500	19.2
2	435	20.2
2	390	11.4
2	360	8.2
3	875	95.2
3	820	89.6
3	750	90.2
3	690	61.6
3	675	74.8
3	550	59.4
3	500	30.5
3	500	29.0
3	380	12.6
3	310	7.7
3	250	9.1
4	875	96.1
4	750	92.0
4	700	62.6
4	670	83.2

13.

Ore No.	Temp.C.	% Loss of Silver
4	550	20.6
4	535	41.2
4	520	49.2
4	470	16.2
4	390	18.5
4	230	7.9
5	975	96.6
5	750	94.3
5	690	76.1
5	570	72.3
5	535	64.3
5	430	19.3
5	355	15.5
5	230	7.1
6	820	33.6
6	800	55.4
6	690	25.2
6	670	19.3
6	540	21.2
6	510	15.8
6	460	23.8
6	365	23.9
7	780	26.2
7	750	28.2
7	690	55.3
7	515	25.5

Ore No.	Temp.C.	% Loss Silver
7	460	7.5
7	440	13.7
7	315	17.8
7	300	9.1
8	780	13.6
8	750	17.3
8	645	9.5
8	590	7.9
8	500	11.1
8	480	21.2
8	440	11.0
8	365	13.2
8	320	16.8
9	750	26.0
9	690	21.3
9	645	33.5
9	560	9.2
9	500	23.1
9	435	15.8
9	365	27.0
9	340	10.9
10	750	36.2
10	720	19.8
10	670	22.8
10	560	17.5
10	560	13.2
10	550	15.9
10	350	20.4

As may be seen from this table the results are not consistent enough to draw any sweeping conclusions.

Literature on the subject is scarce; and all of the articles, that have been published discuss results obtained in actual practice. For this reason these articles give little information in regard to the problem under investigation.

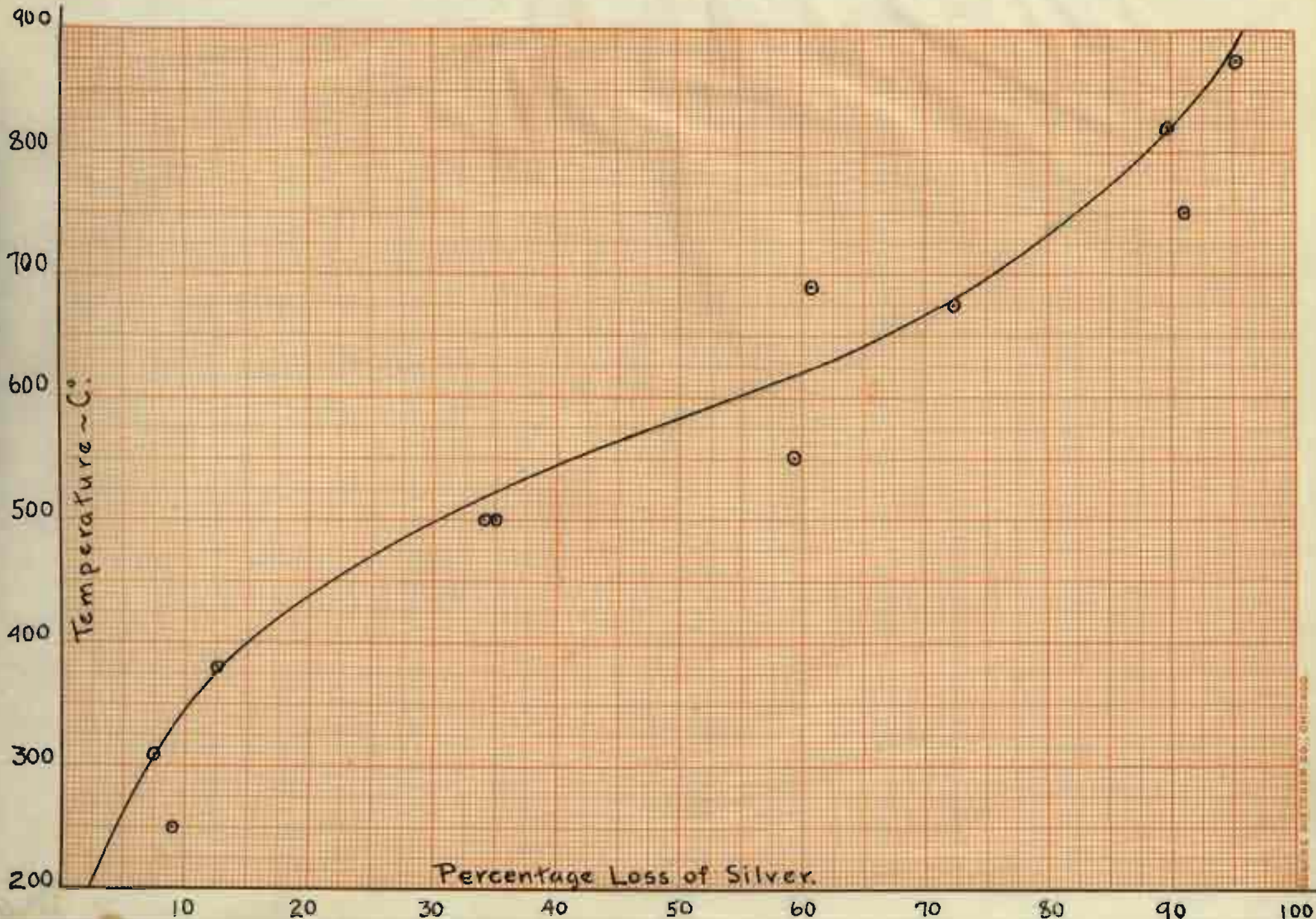
The curve shown on the following page is a temperature-percentage loss curve plotted from the data on ore number three.

The result obtained with ore number one, of pure silica, show that the loss of silver begins at low temperatures, and increases proportionally with the temperature.

In the case of ore number two, of pure calcite, the loss of silver is not excessive until the temperature is raised to about 600 degrees C. At ~~this~~^{this} point the loss in silver is greatly increased, until at 800 degrees about 95 percent is driven off. This rapid increase above 600 degrees is probably due to the dissociation of the calcite and consequent evolution of carbon dioxide.

Since a very high volatilization of silver chloride takes place in the presence of calcite, a method of ore treatment is suggested which may prove practical.

A method of chloridizing roasting is mentioned by Collins, in which the ore is first given a dead roast. This is followed by an addition of sand and salt and the ore again roasted to chloridize the silver. In the last roast a sodium silicate is supposed to be formed, and the chlorine is liberated. It is claimed that this process gives a very complete chloridization, but also a high loss of silver is to be expected.



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If, instead of chloridizing the silver ore with the intention of subsequent amalgamation or leaching, we should roast the ore under conditions favorable to a maximum volatilization of silver compounds; and if this silver can be caught we will secure a very complete extraction of silver at a low cost.

From the results of these experiments it is seen that 96 percent of the silver is volatilized in the presence of Calcite at a temperature above 800. It should be possible to condense and catch this silver in suitable chambers or bag houses. The volatilization might be effected by a modification of the process described by Collins. Let the ore be given a dead roast to remove the sulphur. Then add limestone and salt, and continue the roast at a high temperature. It may be impossible to apply such a scheme in practice, still the results of these experiments point strongly to its feasibility.

If the process is practicable it would certainly be much cheaper than the present practice of chloridizing the ore and then removing the silver by amalgamation or leaching.

In this process the silver would be removed from the ore in one operation. Less handling of ore would be necessary than in the leaching processes.

Fuel to produce the additional temperature would be cheaper in nearly any locality than quicksilver, cyanide or hyposulphite. The recovery would amount to at least 90 percent of the silver contained in the original ore. This is better than the usual extraction obtained in leaching or amalgamation plants, where the ore must be given a previous chloridizing roast. The product from the furnace would be in ^{as} ~~A~~ convenient ^A form to refine ^{as} ~~as~~ of any

precipitate from a leaching plant.

The influence of pyrite on the loss of silver is a striking one. Ores number 6 to 10 contain pyrite in varying percentages. The data is not consistent enough to plot curves, but it may be seen from the table that in all cases the loss of silver in the presence of pyrite is comparatively low. Even at the highest temperatures the loss is less than 30 percent, with the exception of a few cases where mechanical losses occurred.

The small loss when pyrite is present is probably due to reduction of the silver chloride to metallic silver by the sulphur and sulphurous oxide. The reduction apparently takes place early in the roast, because the loss of silver is no greater at high temperatures than at the lower ones.

On account of this effect of pyrite on the volatilization of the silver, it is evident that any treatment according to the scheme proposed on page 15 must be preceded by a complete oxidizing roast.

This concludes the discussion of the results of these experiments, and a brief summary of the points brought out will now be given.

- 1 Prepared silver chloride may be easily pulverized after the addition of a very small amount of ammonium hydroxide.

2. Silica exerts a more or less neutral effect upon the volatilization of silver chloride.

- 3 Calcite tends to rapidly increase the loss of silver at temperatures above 600 degrees C.

4 Pyrite at all temperatures and in any amount tends to greatly reduce the loss of silver.

5. A scheme of treatment is proposed in which the ore is given a dead roast followed by a chloridizing roast in the presence of limestone. The object of the process is to volatilize as much silver as possible. This is to be caught and refined.