THE VOLATILIZATION OF IMPURITIES FROM ZINC CONCENTRATES.

by

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Methods of Analysis:

Introduction

In the present-day treatment of complex zinc sulphide ores by means of differential or selective floatation, or gravity concentration, we secure a product, relatively high in zinc, which, thru usage, has come to be known as zinc concentrates. Hence, in the present dissertation, the term zinc concentrate will be used to designate that product secured by differential floatation or gravity concentration, of the complex lead-zinc, lead-iron-zinc, and lead-iron-copper-zinc ores (most of which contain also varying amounts of both gold and silver) as are mined in the Park City, Tintic, and Bingham districts of Utah, and subsequently treated to separate as far as feasible economically, the various valuable metals from each other and from the gangue materials. The ore so treated is usually of such low grade as to render it valueless unless milled, and the metals (usually present as the sulphides) so intimately intermixed that a complete separation by floatation or gravity concentration is, practically speaking, impossible. Today, the majority of these ores are treated by floatation, and the trend is definitely away from gravity concentration, so this treatise, while recognizing the presence of gravity concentration, will concern itself with floatation products primarily. Floatation so concentrates certain portions of the ore as to give one of the metals a predominent percentage of the total, and this gives rise to the term 'concentrate' as applied to that metal, this concentrate being an economic source of that particular metal.

In the concentration phase, complete separation is not secured, owing to the intimacy with which the various valuable metals are intermixed, and also due to the fact that floatation is not a perfect means of separation of the metals. A glance at Table I, page 9, or Budgen,(1) will show the usual impurities, in about representative quantities. On the whole, however, these impurities may vary between very wide ranges.

However, we are concerned only with those impurities which are harmful in the zinc during the reduction, or when it is present in the metallic zinc---namely sulphur, cadmium, lead, iron, and aluminum. The sulphur is troublesome in the retorting process, each gram of sulphur holding two grams of zinc from reduction, while specifications for spelters cover the other impurities. For these specifications, I refer you to Hofman.(2) Other impurities are present in negligible quantities, but due to the peculiar pyrometallurgy of zinc, only lead and cadmium are troublesome in the retorting process, the iron accumulating from improper handling, according to Hofman.(3) Aluminum was added to the specifications, as .01% of that element makes certain grades of brass useless.(4) In the retorting process, aluminum has no chance to be found in the spelter, as its volatilization is very low, and coke reduces it under only very special conditions. The aluminum in spelter usually comes from the

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(1) Budgen, N.F. Cadmium, its Metallurgy, Properties, and Uses, p4. Lippincott & Co. Philadelphia. 1924.

(2) Hofman, H.O. Metallurgy of Zinc and Cadmium, 1st edit. p 14. McGraw-Hill, N.Y. 1922.

(3) Ibid, p 19.

(4) Stone, G.C.; Bassett, W.H., and Price, M.N. Grades and Uses of Spelter. Eng. & Min. Jour. v.102 p 331 (1916)

aluminum cathodes used in the electrolytic process. In the electrolytic process, only cadmium gives much difficulty;(1) however in both the leaching for the electrolytic proceedure, and during the retorting process, the presence of waste material is detrimental.

Fifteen years ago, the only process of zinc reduction was the retorting process, and that process seemed to be secure in its future. Ingalls(2) voices his opinion that the electrolytic process was a negligible factor, in 1915. During the World War, however, the necessity for exceedingly pure zinc for small arms ammunition arose, and with this as a nurse to the electrolytic process, with its exceedingly pure product, it reached the first stages of maturity, and has continued during the following years to grow steadily; meanwhile the retort processes are merely holding their own, and increasing but little, as the data given by The Mineral Industry during 1928 will reveal.(3) Today, the electrolytic plants are producing at full capacity, while the retort plants are using only one-half to two-thirds of their rated capacity,(4) although the retort process is still the dominent producer in the United States.(3)

The market today is being flooded by zinc as a by-product from the differential floatation from lead and copper ores--both of these metals being much in demand, while zinc is more or less a drug on the market. This will be produced as a by-product as long as lead and copper can be marketed at a profit, so research is needed to expand zinc utilization.

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(1) Liddell, D.M. Handbook of Non-Ferrous Metallurgy, 1st edit. p 1116
McGraw-Hill, N.Y. 1926.

(2) Ingalls, W.R. Electrolytic Zinc. Met. & Chem. Eng. v.14, p 264-5 (1916).

(3) Mineral Industry during 1928 v.37 p 624. McGraw Hill, N.Y. (1929).

(4) Croasdale, Stuart. Hydrometallurgy at the Advent of 1929. Min. Cong.
Jour. v. 15 p 29 (1929)

Whereas before 1915, the retorting industry was well content with its process, today, due to the pressure from the exceedingly pure electrolytic zinc, not infrequently running 99.95% pure,(1),(2) they are beginning to cast about for methods of meeting this purity, or face the ultimate possibility of being forced out of the market. For this reason, they would probably welcome even a radical revision of their process in order to meet the competition of the electrolytic zinc producers.

Too, the purer grades of zinc command a premium, averaging about 4.5% of the price of Prime Western Spelter during the years 1924-28, calculated from data on prices given in the Mineral Industry during 1928.(3) This premium is not enough to cover the costs of a second distillation, but might be used to yield a good profit if means of purification of the ore or spelter could be devised, that was relatively cheap. Too, the demand for pure zinc will continue to increase, as the market learns that the pure metal yields itself to fabrication more easily than the less pure spelter to which it has been accustomed, the final composition of its wares being less variable, and the results therefore more certain; while in alloying, the desired alloys can be produced with more certainty, and greater assurance of success.

Cadmium is today beginning to loom as a valuable by-product, too. Within the last three years, its production has reached the proportions of a million dollar a year industry. Statistics(4) released by the U.S. Bureau

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(1) Tainton, U.C. The Sullivan Electrolytic Plant. Eng. & Min. Jour., v. 126, p 856 (1928)

(2) A.E. Wiggin and R.B. Caples, Electrolytic Zinc Practice at Great Falls, Mont. Eng. & Min. Jour. v. 128 p 319-324 (1929).

(3) Loc. Cit. p 624.

(4) Loc. Cit. p 71. Cadmium, by D.A. Roush.

of Mines show that in 1928, 1,875,896 pounds were produced in the United States, valued at $1,144,297.00, or about $0.612 per pound. This cadmium is entirely a by-product of the zinc and lead industries,(1),(2) cadmium always being present in zinc ores to an amount of a few hundredths of one percent, and is found in the fume from lead smelting operations. There are no commercially worked deposits, the only ore, Greenockite (CdS) being an exceedingly rare mineral.(3) The greenockite is so intimately intermixed with the sphalerite in the native state to defy microscopic detection. Hofman(4) states that the cadmium is present in the ratio of about 1 part of cadmium to 200 parts of zinc—a statement my experiences indorses. (Table I).

Cadmium is employed in alloys, to make them more maleable and ductile; in dentistry, for amalgam fillings; some of its salts are used in medicines, most of its soluble salts being very poisonous; in pigments, as cadmium yellow or cadmium sulphide; and of late, as a protection against rust.(1)

Cadmium plating has come into prominence because of its connection with the automobile and radio industries, and this factor is the reason that the abnormal growth since the war has taken place.(5) Experiments upon the rust resisting properties of steel plated with a thin coat of cadmium is reported by Ed. W. Feldman.(6) In experiments upon the comparative resistance of nickel,

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(1) Wichman, F.M. Cadmium, its Character and Uses. Min. Review, Nov. 15, 1929.

(2) Budgen, N.F. Loc. Cit. p 8.

(3) Ingalls, W.R. Loc. Cit. p 584.

(4) Hofman, H.O. Loc. Cit. p 318.

(5) Mitchell, W.E. Electrolytic Cadmium Plant of Anaconda Copper Mining Co. at Great Falls, Mont. Tech. Pub. #320, A.I.M.M.E.

(6) Feldman, Ed. W.; Metallwaren-Ind. u. Galvano-Tech. v.26 p 8-9 (1928). Also: Jour. Inst. Metals, v. 39 p 589.

zinc and cadmium, rust was produced on the nickel-plated articles after two hours; on hot zinced articles after 650 hours, but not on the cadmium plated articles after 1860 hours. Cadmium alloys are somewhat important. Chief among these is the alloy with copper in telephone and trolley wires. In proportions of .5 to 1.2%, cadmium adds materially to the strength and wearing qualities of the wire.(1)

The lead in the zinc concentrates is more likely to be present for reasons of mechanical occlusion, rather than the semi-chemical combination in which the cadmium is held by the zinc. In treating a complex lead-zinc ore, it is easily seen that mechanical occlusion and incomplete separation by floatation can easily account for the low percentages of lead present. Its presence in retorts is undesirable, due to the slagging action. This is noticeable above 3% lead if the retorts are hard-driven, and above 8% in any case.(2) Lead is not a serious question to the electrolytic production, as sulphuric acid precipitates insoluble lead sulphate, and the residues from the leach is subsequently treated for lead. Lead is a well-known commercial metal, with a definite market at all times.

In the separation of zinc from lead and cadmium, without complicating the proceedure beyond commercial limits, the possibility of volatilization of these as the oxides in the roasting process prior to either the retorting process or electrolytic precipitation, and the subsequent collection of these metals in the fume presents an alluring possibility. Volatilization is the raising of the vapor pressure of the metallic compounds to a temperature where the vapor pressure becomes high, and removing this vapor

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(1) Mitchell, Loc. Cit. p 3.

(2) Ingalls, Loc. Cit. p 503.

by convenient means. In this way, the entire compound can be removed in a definite time. R. Hoffman(1) gives the following data upon the temperatures of volatilization of various compounds of the elements under consideration:

Table II.

Volatilization Temperatures of Pb, Cd, and Zn Compounds.

Oxides:	ZnO	$CdO-CdSO_4$	$PbO-PbSO_4$
Volatilization Temp.	1400°C	700°C	950°C
Sulphides:	ZnS	CdS	PbS
Volatilization Temp.	1180°C	980°C	1085°C
Elements:	Zn	Cd	Pb
Boiling Point	930°C	776°C	900°C (?)
Melting Point	419.4°C	320.9°C	327.4°C

Assuming the above table to be correct, and that we have only the oxides and sulphides present, and that we can maintain a temperature so that its variations will not be greater than 100°C, all of which conditions can be maintained or proven in practice, it would seem that at a temperature of 1100°C, it should be entirely feasible to volatilize most of the lead, and all of the cadmium from a given sample of sphalerite.

From another viewpoint, the roasting and volatilization of the sulphur, lead, cadmium, and adhering moisture would reduce the weight, and hence the freight costs about 25%, thus saving a considerable amount of money if the distance of shipment of the concentrates to the place of

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(1) Hoffman, R. The Waelz Process. Tech. Pub. # 69, Trans. of the A.I.M.M.E. v.76 p 537 (1928).

smelting or precipitation is great. Too, considerable value can be obtained from the fume in the form of lead and cadmium, which in other events would be lost to the producer.

It is, therefore, upon the consideration of (1) cheapening the freight rates, (2) collection of a valuable by-product, and (3) improving the quality of the primary product, that the experimental work of this thesis is based.

Table I.

Analysis of zinc concentrates.

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	A	A	A	A	B	C	D	E	F	G
Zinc	58.26%	59.00%	29.00%	48.80%	51.2%	56.1%	48.3%	44.4%	53.1%	53.42%
Cadmium	.304	.058	0.30	0.05	.19	.35	.51	.11	-	-
Lead	.700	.293	trace	6.12	3.0	1.86	6.34	2.40	5.0	5.3
Iron	2.230	1.900	15.30	8.55	6.0	1.05	6.0	-	3.0	4.0
Copper	.049	.054	2.18	0.33	0.60	1.56			.68	.54
Sulphur	30.42	31.30	31.10	27.30	31.85	30.69	31.05	27.24	28.7	29.7
Insoluble	3.95	6.97	1.75	6.30	2.3	2.12		1.79	5.1	3.8
Silver (oz.)	-	-	-	-	4.0	-	-	-	18.5	20.1
Gold (oz.)	-	-	-	-	.03	-	-	-	.023	.026

Sources: A, from Hofman, Loc. Cit. p 51. B. U.S. Smelting & Refining Co. Local analysis.
C. International Concentrates, local analysis. D. Local Concentrates, Midvale.
E. Local Concentrates, origin unknown.
F and G. Copper and Zinc Ores Treated by Selective Floatation, by B.S. Morrow. E.&M.J. v 128 p 295.

Theoretical aspects of the Problem.

Roasting is the heating of a metal or metallic compound to an elevated temperature, in contact with air, coke, or other reagents, to eliminate one or more chemical components present, thru volatilization as a gas. Roasting is subdivided into a great many parts, such as calcination, oxidation, reduction, and chloridizing roastings. At the offset of this thesis we are concerned only with oxidizing roasting—roasting in contact with oxygen or air; but later we branch into reducing roasting in contact with coke, carbon monoxide, or the sulphide ore.

Volatilization is accomplished by heating the metal or metallic compound to such a temperature that its vapor pressure is sufficiently high, when the vapor is constantly removed by some means (such as a current of air) so the vapor pressure never reaches its equilibrium point, and the compound or metal will be entirely removed in a stated time. Hence, to accomplish volatilization, we must consider (1) the compounds present, and the probability of their occurrence, (2) the effect of high temperatures upon these compounds, as to (a) their melting, or fusion points, (b) their dissociation at the temperatures involved, (c) the vapor pressures of these compounds, and (d) discover from the literature the experiences of others in the volatilization of the compounds previously determined as likely to be present.

The roasting of zinc concentrates requires high temperatures at the offset of the process, but once ignited, the oxidation of the sulphides present furnish practically all of the heat needed to complete the process. Bray gives the ignition temperatures of several minerals, among which are the three chief sulphide materials present in the zinc concentrates:(1)

Table VII.

Ignition point of Sulphide Ores, Centigrade Scale.

Mineral	Grain 1 mm in size	Grain 1-2 mm in size	Grain above 2mm in size
Pyrite	325°C	405°C	472°C
Sphalerite	647	-	810
Galena	554	-	874

As the average zinc concentrate used was 95% -100 mesh, or smaller than .148 mm., it can safely be assumed that the ignition point of the ore was in the neighborhood of 650°C. This temperature must be attained by supplying heat from exterior sources; however, once ignited, the sulphides of zinc (the predominent constituent) react as follows:(2)

$$2\ ZnS + 3\ O_2 = 2\ ZnO + 2\ SO_2.$$

$$ZnS + 2\ O_2 = ZnSO_4.$$

Considering the thermal reactions of the above compounds, we have the following results:

$$ZnS + 3\ O = ZnO + SO_2 - 114{,}550\ cal.^{(3)}$$

$$ZnS + 4\ O = ZnSO_4 - 187{,}720\ cal.^{(3),(4)}$$

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(1) Bray, J.L., Principles of Metallurgy, p 57. Ginn & Co. Boston. 1929.

(2) Hofman, H.O. Loc. Cit. p 73.

(3) Ingalls, W.R. Loc. Cit. p 40.

(4) Getman, F.H. Outlines of Theoretical Chemistry, p343. 4th Edit. 1927. Wiley & Sons, N.Y.

These reactions will supply the heat to reduce the sulphide sulphur to 8-10%, after which it is necessary to add heat from exterior sources, or sinter on a Dwight-Lloyd sinter, to complete the reduction of the sulphur down to 1-2%.(1) Bray(2) states that it is common practice to use one ton of coal to a ton of concentrates during the roasting process.

During the oxidizing roasts, therefore, it would seem that 650°C will be the lower limit of possibilities for roasting. However, to complete a theory of the volatilization possibilities of both lead and cadmium, we must study their reactions in the oxidizing roasts:

$$\mathrm{CdS} + 3\mathrm{O} = \mathrm{CdO} + \mathrm{SO_2} - 101{,}210 \text{ cal.}$$

$$\mathrm{CdS} + 4\mathrm{O} = \mathrm{CdSO_4} - 185{,}550 \text{ cal.}$$

$$\mathrm{CdSO_4} = \mathrm{CdO} + \mathrm{SO_3} + 61{,}700 \text{ cal.}$$

$$\text{or } \mathrm{CdS} + 4\mathrm{O} = \mathrm{CdO} + \mathrm{SO_3} - 123{,}850 \text{ cal.}$$

The heats of reaction in the above list of reactions was calculated from the Handbook of Chemistry and Physics,(3) while Budgen(4) discusses the reactions. Similarily, lead reacts in the following manner,(5) the thermal values also being computed from the Handbook of Chemistry and Physics.(3)

$$\mathrm{PbS} + 3\mathrm{O} = \mathrm{PbO} + \mathrm{SO_2} - 99{,}200 \text{ cal.}$$

$$\mathrm{PbS} + 4\mathrm{O} = \mathrm{PbSO_4} - 195{,}900 \text{ cal.}$$

$$\mathrm{PbSO_4} = \mathrm{PbO} + \mathrm{SO_3} + 74{,}000 \text{ cal.}$$

$$\text{or } \mathrm{PbS} + 4\mathrm{O} = \mathrm{PbO} + \mathrm{SO_3} - 121{,}900 \text{ cal.}$$

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(1) Liddell, D.M. Loc. Cit. p 1203.

(2) Bray, J.L. Loc. Cit. p 268.

(3) Handbook of Chemistry and Physics, 9th edition, pp364-82. Chemical Rubber Co. Cleveland. 1922.

(4) Budgen, Loc. Cit. p 12.

(5) Mellor, Treatise on Inorganic and Physical Chemistry, v 7 p 497. Longmans, London. 1927.

Also:(1

$$ZnSO_4 = ZnO + SO_3 + 52,900 \text{ cal.}$$

$$\text{or } ZnS + 4\,O = ZnO + SO_3 - 134,820 \text{ cal.}$$

From the above equations, we can easily see that we are concerned with nine principle products in the oxidation roast--ZnS, CdS, PbS, $ZnSO_4$, $PbSO_4$, $CdSO_4$, ZnO, CdO and PbO. While recognizing the presence of silicates, and other compounds, the ones mentioned are undoubtedly the principle ones. As the above reactions show, tremendous quantities of heat are liberated during the roasting process. While considerable amounts of this heat is otherwise utilized, it should be possible to utilize the excess to volatilize out a portion of the impurities.

What will be the physical and chemical effects of heating the above compounds to above 800°C? Of the physical effects, the ones most commonly encountered are the raise in vapor-pressure, approaching the melting-point, sublimation-point, and even the boiling point of the compounds. The chief chemical effect is dissociation of certain of the compounds above the temperatures noted. Let us, therefore, consider each of these effects on each of the individual compounds noted above. It might also be of interest to discover the recorded facts upon the volatilization of the various compounds.

The melting point or fusion point of the materials in question will be given the first consideration. If the charge is allowed to fuse, the area exposed to volatilization will be lowered, which will materially effect the rate of volatilization. Too, the probability of the inter-reaction of the various slag-forming compounds within the charge is

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(1) Ingalls, Loc. Cit. p 29.

facilitated. For these reasons, we must keep the mass below the fusion point, or at the greatest, at a point of incipient fusion. The following table has been secured from the literature:

Table VIII.

Fusion Points of Compounds Formed During Roasting.

Compound	Melting-Point	Compound	Melting-Point
PbO	880°C(1) – 893°C(5)	$ZnSO_4$	Decomposed.
PbS	1050 – 1100(3)	CdO	Not Recorded.
$PbSO_4$	Above 1100°(2)	$CdSO_4$	Dec. 1000°
ZnO	Not Recorded	CdS	1750 at 100(4) Atmos. Pressure
ZnS	1900 at 100 Atmos.(4) Pressure		

Mellor(6) states that both CdO and ZnO are highly refractory.

Evaluating the above table, it is easily seen that we will have no trouble with the zinc salts, but lead oxide unvolatilized is likely to cause trouble. Experience upon this point, however, has shown the average point of incipient fusion to be in the neighborhood of 1150°C; while the melting-point of the mass is in the neighborhood of 1300°C. (See Test 8, experimental data)

not [illegible] very [illegible]

Getman(7) shows that every solid has a definite pressure tending to break it up into simpler compounds, called the dissociation pressure.

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(1) Mellor, Loc. Cit. V.7 p 647.

(2) Ibid, v.7 p 807.

(3) Ibid, v.7 p 786.

(4) Ibid, v.4 p 597 (1923 Edit.)

(5) Feiser, Uber die Fluchtigkeit von Blei, Zink, Zinn, und Cadmia. Metall Und Erz, June 1st, 1929. p 271.

(7) Getman, Loc. Cit. p 384.

(6) Mellor, Loc. Cit. p 512, v.4.

Applying this phenomona to the problem at hand, upon each of the components noted above, we find:

The sulphates are the ones most quickly broken down with heat. The International Critical Tables (1) states that at 740°C, the following reaction takes place:

$$ZnSO_4 = ZnO + SO_3.$$

Hofman (2) gives the disintegration series as follows:

$$ZnSO_4 \overset{720^\circ C}{=} 3ZnO.2SO_3 \overset{767^\circ C}{=} ZnO + SO_3$$

Mellor (3) gives the dissociation pressure and temperatures of $ZnSO_4$ as:

°C =	675	690	720	750	775	800
Pmm =	5	6	24	61	112	189

Mellor (4) also states that the dissociation temperature of zinc sulphate is lowered if zinc oxide is present.

According to Budgen, (5) cadmium sulphate decomposes as follows:

$$CdSO_4 \overset{627^\circ C}{=} 5CdO.SO_3 \overset{878^\circ C}{=} CdO + SO_3$$

Oldright (6) notes that lead sulphate begins to decompose to the oxide around 900°C, while Mellor (7) puts the range of temperatures at 900-1000°C.

In the roasting of lead sulphide, several oxides have an

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(1) International Critical Tables, v.6 p 118.

(2) Hofman, H.O. Loc. Cit. p 41.

(3) Mellor, Loc. Cit. v.4 p 602.

(4) Ibid, v.4 p 619.

(5) Budgen, Loc. Cit. p 12.

(6) Oldright, G.L. Lead-Zinc Separation by Volatilization. Reports of Investigation # 2544, U.S. Bur. Mines. 1923.

(7) Mellor, loc. cit. v.7 p 807.

opportunity to form—PbO, Pb_3O_4 and PbO_2 being some that might under ordinary or extraordinary conditions be present. Assuming these present, we will determine their behavior toward heating:

$$(1) \quad Pb_3O_4 = PbO + O_2$$

according to Mellor,(1) who gives the following table on the dissociation pressures of this oxide:

^oC	=	444.8	464.4	511.2	537.6	558.3
p_{mm}	=	8.4	30.4	76.0	155.	270.

As the partial pressure of the oxygen in the atmosphere at 760 mm. is about 159 mm., it can be seen that this oxide will cease to exist after the temperature has been maintained above 540°C for any length of time. Mellor(1) also gives the formula for the dissociation to be:

$$\log_{10} p = -7.8595\, T^{-1} + 11.8976.$$

$$(2) \quad 2\ PbO_2 = 2\ PbO + O_2.$$

Mellor(2) reports that the above reaction has a pressure of .21 atmosphere (Partial pressure of the oxygen in the atmosphere) at 394°C. From these two facts, PbO, of these, alone, would probably exist as the oxide above 550°C.

Mellor(3) reports the presence of the suboxides of both cadmium and zinc, but the consensus of opinion is that it is a mixture of both the metal and the oxide, rather than a definite compound. These would be immediately oxidized in contact with the air to the full oxides. The dissociation pressure of zinc oxide is:(4)

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(1) Mellor, Loc. Cit. v7 p 675.

(2) Ibid, v.7 p 684.

(3) Ibid, v.4 p 505.

(4) Ibid, v.4 p 512.

$^{\circ}C$ = 227 1227 1727

p_{mm} = $0.0_{66}1333$ $0.0_{16}3670$ $0.0_{10}9489$

which at once shows this to be a negligible factor. A. Colson(1) states that CdO dissociates below 600°C, and the volatilized film of Cd forms in transmitted light a violet-blue film on the walls of a glass vessel, but Budgen(2) suggests that this is true only in the presence of the metal. PbO does not decompose below 2075°C.(3)

Cadmium sulphide dissociates at 600°C.(4) Upon the other sulphides, I have no data.

From the above considerations upon the dissociation pressures of the various minerals, it would seem that above 1000°C (the range in which most of the experimental work was carried on, due to vapor pressure considerations taken up later) the sulphate compounds need no consideration, as they are doubtless but transient compounds. We will, therefore limit ourselves to the consideration of only the sulphides and oxides of the metals in question, both of which are present throughout an oxidizing roast; and turn our attention to the vapor pressures of these compounds, to determine at what temperatures volatilization may take place.

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(1) Mellor, Loc. Cit. v.4 p 512.

(2) Budgen, Loc. Cit. p 11.

(3) Mellor, Loc. Cit. v.7 p 648.

(4) Ibid, v.4 p 597.

Studying the sulphides, it was found that the vapor pressure of lead sulphide is at different temperatures:(1)

°C	=	850	917	940	975	980	995
P_{mm}	=	2.0	4.0	6.0	11.9	13.0	17.0

W. Biltz found cadmium sulphide sublimes at 980°C, and zinc sulphide at 1178±2°C.(2) Doeltz and Graumann(2) found zinc blende slightly volatile at 1000, but copiously so at 1200°C. This volatilization of zinc sulphide is apparent but once in my work. (Test #24)

Passing to the oxides, Jensch(3) states that cadmium oxide is volatilized to 61.8% by roasting zinc ores. Budgen(3) gives a graph showing the relative volatility of zinc oxide and cadmium oxide at different temperatures. Mellor(4) states that both zinc and cadmium oxides are volatile at a white heat, but neither at a red heat. Feiser(5) gives a very complete treatise upon the vapor pressures of zinc, lead, and cadmium oxides, and from his graphs have been constructed the composite Graph I. It shows a very alluring possibility of separation of the oxides by temperature ranges between 100 and 1300°C. Feiser(6) also gives the vapor pressures of litharge from 750 to 1470°C, the boiling-point of the oxide.

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(1) Mellor, Loc. Cit. v.7 p 736.

(2) Ibid, v.4 p 597.

(3) Budgen, Loc. Cit. p 11.

(4) Mellor, Loc. Cit. v.4 p 511.

(5) Feiser, Loc. Cit. pp 269-84; Figures #95, 100 and 101.

My own experiences in the experimental work has corresponded to Feiser's results much more closely than to the other authorities mentioned.

Upon the quantity of material volatilized at any one temperature, considerable data can be obtained from the literature, but at its best, a larger portion of it is contradictory. Mellor(1) gives the following quantities of lead oxide volatilized during the period of one hour at different temperatures:

°C	700	800	900	950	1000
% Volatilized	.1	.2	2.0	5.0	10.0

and further states that the volatilization rate is lowered by silica or hematite. Feiser(2) also gives the amount volatilized in 30 minutes--100 percent above 1200°C, also checked in this work.

Upon the rate of volatilization of zinc oxide, Mellor(3) gives the following data, however no time limit is specified:

°C	1000	1200	1300	1400	1700
% Volatilized	Very Little	Begins	1%	13%	Very Rapid

Feiser(4) gives the quantity of cadmium oxide volatilized in 30 minutes from 128.14 grams, 30 cm² surface exposed, as:

°C	900	1000	1100	1200
Gm. Volt.	.0001	.0016	.0121	.0876

Seemingly, this rate is materially lowered by the presence of hematite.

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(1) Mellor, Loc. Cit. v.7 p 647-8.

(2) Feiser, Loc. Cit. p 279.

(3) Mellor, Loc. Cit. p 597, v.4.

(4) Feiser, Loc. Cit. p 273.

When we consider the effect of addition of coke to the roasted ore, in order to volatilize further amounts of both cadmium and lead, we encounter the following reactions in the literature:(1)

$$CdO + C = Cd + CO.$$

$$CdO + CO = Cd + CO_2.$$

$$2\,CdO + C = 2Cd + CO_2.$$

These reactions start about 580°C, and over 1% of cadmium is volatilized at 700°C. Hofman(2) states that in practice, the figures are from 702 to 813 for the reduction of cadmium to the metal by coke. Hofman(2) says the following reactions:

$$ZnO + C = Zn + CO.$$

$$ZnO + CO = Zn + CO_2.$$

$$CO_2 + C = 2\,CO.$$

$$2\,ZnO + C = 2\,Zn + CO_2.$$

have a practical range of 1022 to 1088°C. The boiling-point of cadmium is 778°C, and for zinc, 930°C, so we have a practical range of 150°C in which the separation may be carried out. O'Hara(3) finds that carbon dioxide in concentrations of 10% practically reoxidized the zinc at 750°C. Mellor(4) reports that the reaction:

$$Zn + CO_2 = ZnO + CO.$$

have their equilibrium points as follows:

°C	=	1000	1125	1500
% CO_2	=	.1	.2	.75

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(1) Budgen, Loc. Cit. p 38.

(2) Hofman, Loc. Cit. p 320.

(3) O'Hara, B.M. Oxidation of Zinc Vapor by Carbon Dioxide. Bur. Mines Tech. paper # 336. 1924.

(4) Mellor, Loc. Cit. v.4 p 413.

C.G. Maier of the Berkeley Station of the U.S. Bureau of Mines has kindly calculated for this work that the reaction:

$$Cd + CO_2 = CdO + CO$$

is prevented by over 95% of carbon monoxide, at 750°C.

The presence of either carbon monoxide or coke with lead oxide would immediately reduce it to its metallic state; carbon monoxide reducing it at 300°C, and litharge is reduced at a dull red heat by charcoal or coke.(1) Lead, however, would not volatilize, as it has a boiling-point of 1525°C.(2)

The effect of coke upon the sulphides is also marked. Mellor(3) finds that when zinc sulphide is heated with coke, it volatilizes altogether, with the probable reaction:

$$2\,ZnS + C = 2\,Zn + \boxed{CS_2}.$$ unstable at high temps

This begins at 1300-1350°C, however my own experiences show a lower point than this. Cadmium sulphide dissociates at 600°C,(3) but no indications are given for its reaction as above. Mellor(3) also indicates that at 750°C, the reaction:

$$ZnS + CO_2 = ZnO + CO + S$$

occurs. Lead sulphide is uneffected by coke, carbon monoxide, or carbon dioxide except at white heats.(4)

There is also the possibility presented by the lead, that there might be an interreaction between the sulphides, oxides, and sulphates:(5)

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(1) Mellor v.7 p 655.

(2) Handbook of Chem & Phys. Loc. Cit. p 107.

(3) Mellor, Loc. Cit. v.4 p 605.

(4) Ibid, v.7 p 792.

(5) Ibid, v.7 p 497.

$$PbS + 2\,PbO = 3\,Pb + SO_2.$$

$$PbS + PbSO_4 = 2\,Pb + 2\,SO_2.$$

However, a search of the literature revealed no interreactions between the salts of cadmium and zinc.

Summarizing the above data, we see (1) that the fusion point of a roast is between 1150 and 1200°C; (2) that sulphates are but of secondary importance; (3) that the vapor pressures can be utilized to differentiate lead and cadmium oxides from zinc oxides between 1000 and 1300°C; and (4) that at about 1200°C zinc sulphide begins to (theoretically) vaporize, while cadmium sulphide begins to volatilize below 1000°C, and that lead sulphide has an appreciable vapor pressure at 1000°C. From the data, the opportune temperatures for volatilization of lead and cadmium salts from zinc compounds would seem to be in the neighborhood of 1100°C. Toward experimentally testing this point, this thesis is aimed. Of the effect of reducing agents, it would seem that temperatures below 1000°C should be utilized, because of the volatilization of zinc oxide thru reduction. Experimentally, however, this temperature was nearer 1100°C.

Methods of Analysis

The analysis of the metals reported in this thesis were made by the following methods:

(1) Zinc.

One-half gram of the sample was dissolved in 10 cc. of HCl and 10 cc. of HNO_3, and taken to dryness. The residue was taken to dryness with another 10 cc. of HCl, and then taken up in 10 cc HCl and 150 cc of water. This was boiled, and then NH_4OH was added to precipitate the iron, 5 grams of ammonium chloride and a small pinch of ammonium persulphate being added to the ammoniacal solution, the former to keep the zinc in solution, the latter to oxidize any manganese present. This was boiled, and filtered. If the precipitate was large, it was dissolved in HCl, and the iron reprecipitated with NH_4OH as above. This was filtered, and the ammoniacal solution mixed. 5 cc. of excess HCl was added, 3 to 5 grams of test lead added, the solution diluted to 300 cc., and the solution boiled until the copper precipitated. The solution was cooled to 70°C, and titrated with a standard ferrocyanide solution, using ammonium molybdate or uranium nitrate as outside indicators.

(2) Lead.

Keefer's volumetric chromate method was used.(1)

(3) Sulphur.

One-half gram sample was moistened, .5 gm. potassium chlorate added, and then 10 cc. of nitric acid. This was fumed slowly to dryness. Ten cc of Hydrochloric acid were added, and the solution again taken

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(1) Keefer, Robert. Methods in Non-Ferrous Metallurgical Analysis, 1st Edit. 1928, p 150. McGraw-Hill, N.Y.

to dryness. Residue was taken up in 5 cc. hydrochloric acid and 140 cc. of water, boiled, and the iron precipitated out by the addition of excess ammonium hydroxide. The iron hydroxide was filtered off, the solution heated to boiling, 5 cc. excess HCl added, and the sulphates formed precipitated by adding excess $BaCl_2$. The barium sulphate was digested on the hot-plate for one-half hour, the solution cooled, filtered thru a hard, ashless filter, and the residue ignited at a red heat. The product, pure, white barium sulphate, was weighed as such.

$$\% \text{ Sulphur} = \text{Weight } BaSO_4 \times .1373 \times 200.$$

(4) Sulphate Sulphur.

The HCl method described by Keefer was employed.(1)

(5) Cadmium.

This determination, with the desired degree of accuracy, was very troublesome, because of the high zinc content as compared to that of the cadmium—50 to 60% of zinc being present to from .1 to .5% cadmium. The methods employed in various texts on qualitative analysis were tested and found to be very unsatisfactory. The proceedures of several Western Smelters were also tried, and while better suited to the problem at hand, did not prove entirely satisfactory, as they were designed for higher percentages of cadmium than were present here.

The chief difficulty in any of these determinations was the length of time required for the determinations, and the number of steps taken in the analysis. Too, the degree of accuracy was designed to be within .2% of correct—and a large portion of the work covered analysis of materials holding less than this limit of error. After about four months

Mines tot
Cd Conte
Lo

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(1) Keefer, Loc. Cit. p 243.

of experimentation, it became evident that if the problem was to be satisfactorily solved, a method would have to be evolved that would shorten the time, but primarily give an accuracy of not less than .05%.

The separation of cadmium from copper and zinc caused the most trouble; especially the zinc-cadmium separation. Also, the actual evaluation of the purified cadmium solution caused some difficulty.

In most cases cited in the literature, zinc was separated from cadmium in a slightly acid solution, but this was especially time-consuming, and required considerable equipment. An idea may be gathered from the fact that it required from one to two hours constant gasing with hydrogen sulphide to be reasonably sure that all the cadmium was precipitated; quite often even then, I rather think that the cadmium was not precipitated, due to the presence of ammonium salts, which materially effect the precipitation of cadmium sulphide. Directions were rather vague as to the range of acid concentration over which cadmium sulphide was precipitated, and inexpert manipulation would probably give erroneous results for this reason.

The separation of cadmium from copper was the source of the most readily detected errors. Several methods were tried: The first depended upon the solubility of cadmium sulphide in boiling 1 : 5 sulphuric acid, and the insolubility of copper sulphide in the acid of that strength; however, as demonstrated later, the probability is that cadmium sulphide is not quantitatively soluble in even hot, concentrated sulphuric acid. Another method tried was the precipitation of copper sulphide from the solution while boiling with a solution of sodium thiosulphate. Within my own experiences, I find that cadmium sulphide is precipitated in this solution. The following experiment shows this: Dissolving 1.3886 grams of pure stick cadmium in nitric acid, taking to sulphur trioxide fumes with hydrochloric and sulphuric acids, dissolving the cadmium sulphate in 150 cc. of water, introducing 25 cc. of a 25% hypo solution, a precipitate was formed after boiling 5 minutes. From this precipitate, it was calculated that 1.5% of the cadmium had been precipitated. Mellor is inconclusive on this point; at one place[1] he states that it will precipitate neither cadmium or zinc from their salts; in another[2] he states that it will quantitovely precipitate cadmium sulphide in an acetic acid solution. For my purposes, however, it was rejected. Another method suggested was the precipitation of cadmium sulphide in an ammoniacal solution, with potassium cyanide present to keep the copper in solution, by the use of hydrogen sulphide. Potassium cyanide is a reagent to be used only in the most stringent Cond? positions, because of the liklihood of the solution accidently being made acid, and the deadly fumes of prussic acid evolved.

The actual evaluation of the cadmium was another question which confronted me. The standard practice is electrolytic precipitation, but the labratory did not possess the needed equipment. The evaluation by weighing as cadmium sulphate in a platinum dish, after taking the chloride down to dryness in sulphuric acid, was a long proceedure, very difficult to perform, due to the habit of the acid

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[1] Mellor, Loc. Cit. p 494, vol. 4.

[2] Ibid, p 588, vol. 4.

of erupting violently when heated in a concentrated form, and also due to the platinum ware needed for the determination. One other standard method is the titration with potassium ferrocyanide, as in the method of zinc determination, but this is never successful, even the smelter methods advising against it. The determination of cadmium as the sulphide has been proven to be erronous.(1)

Plainly, the standard methods had been tried, and these methods did not work on this problem. We were faced with the facts—we would have to develop a method for the determination of the cadmium, or abandon the problem. The former plan was adopted, and the literature searched for new methods, or parts of methods and hints that might lead to a satisfactory proceedure. In this manner, a satisfactory, though not entirely perfect method was evolved, with a degree of accuracy on low cadmiums that was in keeping with the nature of the work. Each Phase of this method will be taken up in detail below, followed by a resume of the proceedure as it was finally standardized.

Cadmium Experimental Work.

The usual method for the solution of sulphide ores was employed; no trouble was experienced from this source. The details of this step will be taken up in the resume.

(1) Separation of cadmium from copper, arsenic, antimony and lead. Mellor(2) gives a portion of the electromotive series of the metals in the following order: Manganese, zinc, cadmium, iron, cobalt, nickel, tin, lead, hydrogen, antimony, bismuth, arsenic, copper, mercury and silver.

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(1) Hildebrand and Lundell, Applied Inorganic Analysis, 1929, p 204.
Wiley and Sons, N.Y.

(2) Mellor, Loc. Cit. v.1 p 1014; 1927 Edit.

Each metal in this list will displace all metals following it from solutions of their salts. The second step of the determination was to remove the members of the acid sulphide group (lead, bismuth, copper, and arsenic) by precipitation with iron turnings. In order to have the above displacement take place comparatively rapidly, there must be a gap of four or more members of the series between the two elements concerned, therefore, in this case, lead could not be reduced rapidly, so that it was removed by precipitation with sulphuric acid, as the insoluble lead sulphate. Tin is seldom troublesome, as it practically is never found in appreciable amounts in the zinc concentrates of this district, so this objection is removed. However, it would react similarily to the lead. Copper was present in the largest amounts, with smaller amounts of arsenic, antimony, and bismuth; all of these elements are easily and completely removed by precipitating with iron.

Cadmium, evidently, would not be precipitated by iron, and would remain in solution along with the zinc and such quantities of manganese as was contained in the zinc concentrates.

(2) Separation of cadmium from zinc, iron, and manganese. Ammonium sulphide(1) was selected as the precipitating reagent because a high concentration of sulphide ions can be obtained quickly with the same. Mellor(2) states that cadmium sulphide is sparingly soluble

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(1) Taken from a smelter method

(2) Mellor, Loc. Cit. v.4 p 589.

soluble in ammonium sulphide, is less soluble in the cold than in the hot,(1) and in amounts so small as to be a negligible factor in quantitative analysis.(2) Nevertheless, cadmium sulphide is sparingly soluble in all aqueous solutions of ammonium salts,(3) so that the concentration of the same should be kept as low as possible.

The seperation of cadmium from the other elements in solution (iron, manganese and zinc) and zinc especially, depends upon a careful control of hydrogen ion concentration of the solution. Blasdale(4) states that the solubility product of cadmium sulphide is 5 x 10^{-29} and that of zinc sulphide is 1.1 x 10^{-24}. In order to carefully investigate the optimum hydrogen ion concentration, i.e., the amount of acid that should be added for the best seperation of cadmium from zinc, the following tests were made: One gram of zinc was dissolved in 100 cc. of solution, neutralized, and then quantities of acid were added as noted in the following table. A solution of cadmium was made up and treated similarily; 0.517 gm. of cadmium was used per 100 cc. of solution. Five cc of ammonium sulphide were added to the hot solution, followed by cooling and then filtering off the precipitated sulphide. The zinc precipitated was determined by the standard ferrocyanide method; the cadmium by the pyrophosphate method described later. Note that the zinc was determined seperately from the cadmium; the solutions were not mixed. Table VIII gives the results of the tests.

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(1) Mellor, Loc. Cit. v.4 p 589.

(2) Ibid, v.4 p 605.

(3) Ibid, v.4 p 604.

(4) Blasdale, Fundimentals of Quantitative Analysis, p 122, 3rd Edition. Van Nostrand Co. N.Y. 1922.

Table VIII.

Effect on the precipitation of zinc and cadmium, of the addition of varying amounts of HCl to neutral solutions of zinc (1.0 gm. zinc per 100 cc. of solution) and cadmium (0.517 grams per 100 cc. of solution). Constant amount of precipitating reagent, 5 cc. of ammonium sulphide (light).

Test	HCl added	Gm. Zn in precipitate	Gm Cd in solution.
1	1 drop	.894	.0025
2	1 cc.	.562	
3	2 cc.	.481	
4	3 cc.	.419	
5	4 cc.	.239	
6	5 cc.	.1182	.0018
7	6 cc.	.0066	.0021
8	7 cc.	.0000	.0018
9	8 cc.	.0015	.0008
10	9 cc.	.0010	.0010
11	10 cc.	.0000	.0018
12	11 cc.	.0010	.1110
13	12 cc.	.0015	.1128
14	13 cc.	.0010	.2095
15	14 cc.		.2856
16	15 cc.		.3475

After experimentation had shown that 21 cc. was too strong an acid concentration to use in actual practice, when precipitating cadmium in 300 cc. of solution, it was realized that ammonium sulphide would have a neutralizing action upon the acid, constant in its effect, so the experiment tabulated in Table IX was made. Cadmium (0.4311 gm.) was dissolved in 300 cc. of solution, and varying amounts of HCl was added to the neutral cadmium solution. Next, 5 cc. of ammonium sulphide were added to the hot solution, followed by rapid cooling, the precipitate filtered off, and the cadmium content of the filtrate determined. The following table gives the data upon these tests.

Table IX.

Effect on the precipitation of cadmium, of the addition of varying amounts of HCl to the neutral solution of cadmium (0.4311 gm of cadmium per 300 cc. of solution). Constant amount of precipitating agent, 5 c.c. of ammonium sulphide.

Test	cc HCl added	Gm cadmium in solution.
1.	14	.0011
2.	15	.0014
3.	16	.0003
4.	17	.0008
5.	18	.0008
6.	19	.0020
7.	20	.0026
8.	21	.0575
9.	22	.0462
10.	23	.1503

Tests 3, 4, and 5, of Table IX indicated that the presence of from 16 to 18 cc. of hydrochloric acid per 300 cc of solution was the proper concentration for the nearly complete precipitation of cadmium as cadmium sulphide. Therefore this concentration was used in all subsequent work.

Solution of Cadmium Sulphide

The next step of the procedure was the dissolving of the cadmium sulphide. Mellor(1) states that cadmium sulphide is soluble in boiling 20% sulphuric acid, dilute nitric acid, and in large excess of hydrochloric acid. The solubility of cadmium sulphide in sulphuric acid was tested in relation to this analytical procedure. The stated amount of cadmium metal was weighed out and dissolved in concentrated nitric acid, the solution neutralized, and the cadmium precipitated with five cc. of ammonium sulphide, in a 2% HCl solution. The precipitate was filtered off and digested in boiling 20% sulphuric acid solution for 30 minutes, followed by precipitation of the dissolved cadmium as the ammonium phosphate, igniting and weighing as the pyrophosphate. The data accumulated ~~is~~ are recorded in table X.

Table X.

Amounts of cadmium sulphide dissolved by digesting in 20% sulphuric acid for 30 minutes. Comparison on the basis of grams of cadmium. Cadmium determined by the pyrophosphate method.

Test	Cd Weighed in	Cd Recovered.
1.	.3356 gm.	.3042 gm.
2.	.3222	.2861
3.	.3106	.2932

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(1) Mellor, Loc. Cit. v.4 p 492.

The above work shows that for this proceedure, 20% sulphuric acid is an unsatisfactory solvent. This may be due (1) to the method of final precipitation, but most likely (2) that sulphuric acid is not a quantitative solvent for cadmium sulphide. Dilute nitric acid (25% by volume) was next tried in exactly the same way that the 20% sulphuric acid had been tested. The results are shown in Table XI.

Table XI.

Relative amounts of cadmium sulphide dissolved by digesting in a boiling 25% nitric acid solution for 30 minutes. Comparison on the basis of grams of cadmium. Cadmium determined by the pyrophosphate method.

Test	Cd Weighed in	Cd Recovered.
1.	.3969	.3843
2.	.6097	.5917
3.	.5808	.5746

The results of this test were somewhat better than those of the preceeding one, but the same were not accurate enough for a quantative analysis scheme. The series of tests were repeated with a solution of one volume of nitric acid to two volumes of water; two were taken to nitric oxide fumes, the other to dryness. Conditions otherwise the same as in the preceeding tests, Tables X and XI. The results are given in Table XII.

Table XII.

Relative amounts of cadmium sulphide dissolved by digesting in a 33% (by volume) solution of nitric acid for 30 minutes. Comparison on the basis of grams of cadmium. Cadmium determined as the pyrophosphate.

Test	Cd Weighed in	Cd Recovered	Remarks.
1.	.3737 gm.	.3628 gm.	Taken to dryness.
2.	.4126	.4153	Taken to NO_2 fumes.
3.	.5756	.5770	" " " "

The last two results of the table (XII) gives the required solubility, altho slightly high. Therefore, this proceedure was adopted as the standard for dissolving the precipitated cadmium sulphide.

Determination of Cadmium as the Pyrophosphate

With the purified cadmium solution, various methods for the actual evaluation of the cadmium were noted in the literature. Of these only two will be touched upon, though some others were tried and rejected. Electrolytic precipitation of the cadmium undoubtedly is the most accurate method; for a discription of the proceedure and comparative accuracy, see Miller and Page.(1) An alternative method is the precipitation of the cadmium as cadmium ammonium phosphate with secondary ammonium phosphate, $(NH_4)_2HPO_4$, followed by ignition to cadmium pyrophosphate and weighing the latter.(2) To test the pyrophosphate method, amounts of stick cadmium as stated below, were weighed in, dissolved, and then treated as noted in the preceeding sentence. The results of these tests follow in Table XIII.

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(1) Miller and Page, Columbia School of Mines Quarterly, v. 22 p 391, 1900.

(2) Ibid, p 395.

Table XIII.

Accuracy of the pyrophosphate method for the determination of cadmium. Quantities of cadmium metal, as stated, dissolved in HNO_3, precipitated as cadmium ammonium phosphate, ignited to cadmium pyrophosphate.

Test	Cd Weighed in	Cd Found
1.	.5264 gm.	.5258 gm.
2.	.3960	.3955
3.	.2470	.2465

The above results were quite satisfactory. The procedure as a whole was now applied to synthetic mixtures of the elements which occur in zinc concentrates. The results are given in Table XIV.

Table XIV.

Analysis of cadmium in synthetic mixtures; 4.9110 gm. Cd, 4.9623 gm. Zn, 1.0000 gm. MnO_2, 5.0038 gm. ferrous ammonium sulphate and 5.0004 gm. copper foil were contained in one liter of solution; 25 cc. portions of this solution was used.

Test	Cd in Sample	Cd Recovered.
1.	.1228 gm.	.1240 gm.
2.	.1228	.1255
3.	.1228	.1263
4.	.1228	.1267

The cadmium found was slightly higher than the amount present, due to zinc, so the researches on acid concentration recorded on pp 30-31 were made (Tables VIII and IX). With the acid concentration controlled, the results recorded in Table XV were obtained.

Table XV.

Analysis of cadmium in synthetic mixture of 0.9110 gm Cd.; 5 gm. ferrous sulphate; 5.0076 gm. Cu; 30 gm. zinc sulphate, 1.0 gm. lead acetate, per liter of solution. 10 cc. samples taken.

Test	Cd in Sample	Cd Found.
1.	.0091	.0093
2.	"	.0091
3.	"	.0095
4.	"	.0097
Average	.0091	.0094

These last results were of a degree of accuracy which was satisfactory for the work at hand. The method was then applied to zinc concentrates, and compared with careful analyses by trained men in smelter laboratories. In three cases, this method checked within .01% of their results. The proceedure was therefore considered satisfactory for the investigation. As noted at the beginning of this discussion, a resume of the process would be made, for experimental work.

<u>Proceedure for the Determination of Cadmium.</u>

Weigh out a five gram sample, if the cadmium content of the ore is less than .5%, place in a 400 cc. beaker, add 5 cc. water, 30 cc. nitric acid, and .5 gm. potassium chlorate. Evaporate to dryness. Add 10 cc. HCl, take to dryness. Add 5 cc. of sulphuric acid, and dilute to 200 cc.; heat to boiling, and boil till cadmium cake dissolves. Remove from hot-plate, add 5-7 gm. of clean iron filings, coarse. Allow vigorous evolution of hydrogen to cease, set on the hotplate, and boil until the hydrogen is expelled. Cool the solution, filter, and wash well with water.

Add to the filtrate 15 cc. of HCl, and dilute to within 15 cc of 300 cc. Boil, and add to boiling solution 10 cc of ammonium sulphide. Cool as quickly as possible in a stream of running water, filter off the precipitated CdS, and wash thoroughly. At this point, the filtrate should be tested for cadmium in solution by the slow addition of ammonium hydroxide, a drop at a time, until the zinc begins to permanently precipitate. If CdS forms, filter off in original paper.

Place the filter paper and precipitate in original beaker, add 50 cc of 1 : 2 HNO_3 solution (by volume), break up the paper, and take to fumes of NO_2 on the hotplate, but take exceeding care not to let it go to dryness. Dilute to 150 cc., boil, and filter off the digested paper. Neutralize with ammonia, or better still, sodium hydroxide, using litmus as the indicator. Add 17 cc. HCL (ACCURATE!) and dilute to 300 cc. Heat to boiling, and while boiling, add five cc. of ammonium sulphide. Cool quickly as before. The CdS will be slow in precipitating this time, and the addition of not to exceed 2 cc. of ammonium hydroxide can be resorted to, if the precipitate does not come down. Filter, and test the filtrate with ammonium hydroxide, to faint opalescence (Of ZnS, but no permanent precipitate); allow to stand for 10-15 minutes. This precipitation has been found to be the most troublesome of any of the steps, and it would be well to watch the losses here rather closely. The slowness of the precipitation can be laid at the door of the ammonium salts present, and for this reason it is strongly recommended to use alkali hydroxides, for the previous neutralization. Place the filter paper and the CdS in the original beaker, cover with 50 cc. of 33% HNO_3, and digest to brown fumes as before. Dilute to 125 cc. (fairly accurate) boil, and filter off the paper.

To the filtrate, add a few drops of methyl orange, and take to faint alkalinity with ammonium hydroxide. Add HCl, a drop at a time, until faintly acid, and then 3 drops in excess. Add 2 grams of $(NH_4)_2HPO_4$ and allow to stand overnite ght; filter off the precipitated cadmium ammonium phosphate on ashless filters, wash thoroughly with water, and place in a crucible. Ignite the paper at low heat, and finish off at a red heat. The pyrophosphate formed is stable to above 800°C. Weigh as the pyrophosphate of cadmium, $CD_2P_2O_7$.

$$\text{Wt. } Cd_2P_2O_7 \times .56365 = \text{wt. Cd.}$$

In passing, certain notes should be made upon the proceedure, as a matter of helping ones who try the method:

(1) The iron filings should be fairly coarse; otherwise the reactions will proceed with almost explosive violence.

(2) When adding the ammonium sulphide, stir vigorously.

(3) Never let the nitric acid solution of the sulphide go to dryness, as the filter is reduced to a pasty mass which occludes considerable cadmium.

(4) Cooling quickly adds materially to the quickness of filtering the sulphides, as it seems to avoid the well-known colloidal

state so troublesome when filtering metallic sulphides.

(5) When the cadmium is present in less than .3%, the color of cadmium sulphide cannot be detected in solution, but may be detected on the paper. The solutions of this concentration of cadmium assume a milky appearance in the second precipitation.

While some features of the method are not entirely satisfactory, the method can be relied upon to from .02 to .04%. The author of this thesis has used it for all the analysis of cadmium figures reported in this thesis, and upon this point, the thesis stands or falls. Above all, an average of 15 to 20 cadmium determinations can be made per day, and this speed could readily be increased by experience and continual use of the method.

Apparatus and Manipulation.

The apparatus used in all but two of the experiments is sketched in Figure 1. As this figure shows, a gas-fired assayer's muffle was used for the heating and roasting the charge. The muffle-bottom had a total area of 204 square inches, 17 inches deep by 12 inches wide. The muffle-bottom was protected from the slagging action of the zinc ores by a tight-fitting corundum slab, luted in with fire-clay. This held up well, even at 1200°C. Upon this bottom was spread evenly the 6000 gram ore-charge, which made a depth of approximately one inch.

The fume and gases were drawn from the back of the muffle thru a 1.25 inch pipe, 7 feet long, into the baghouse. The air passing over the mass was removed at a rate fast enough to prevent the escape of fume, but was carefully regulated by valves admitting cold air into the baghouse. This cold blast served two purposes: (1) it cooled and precipitated the fume at the entrance to the baghouse, and (2) it cooled the baghouse an appreciable extent. Especially in the reducing roasts, due to the oxidation of zinc vapor above the bed, the baghouse usually was heated quite hot, necessitating this cooling action of the stream of cold air.

The bag was made of asbestos cloth. Experiments were carried out with cotton bags, but the acid, formed during the reactions, quickly destroyed these bags. The asbestos bags were then substituted, and found to be very efficient, especially after the first run, when they became coated with fume, wetted somewhat with the acids in the gases, and rendered almost water-tight. The bags lasted for a considerable

NO.	PIECE	TYPE
1	Assayer's Muffle	D.F.C. No 4511
2	½ H.P. Motor	Century Single Phase.
3	Exhaust Fan	Victor Blower No 17.
4	Baghouse	

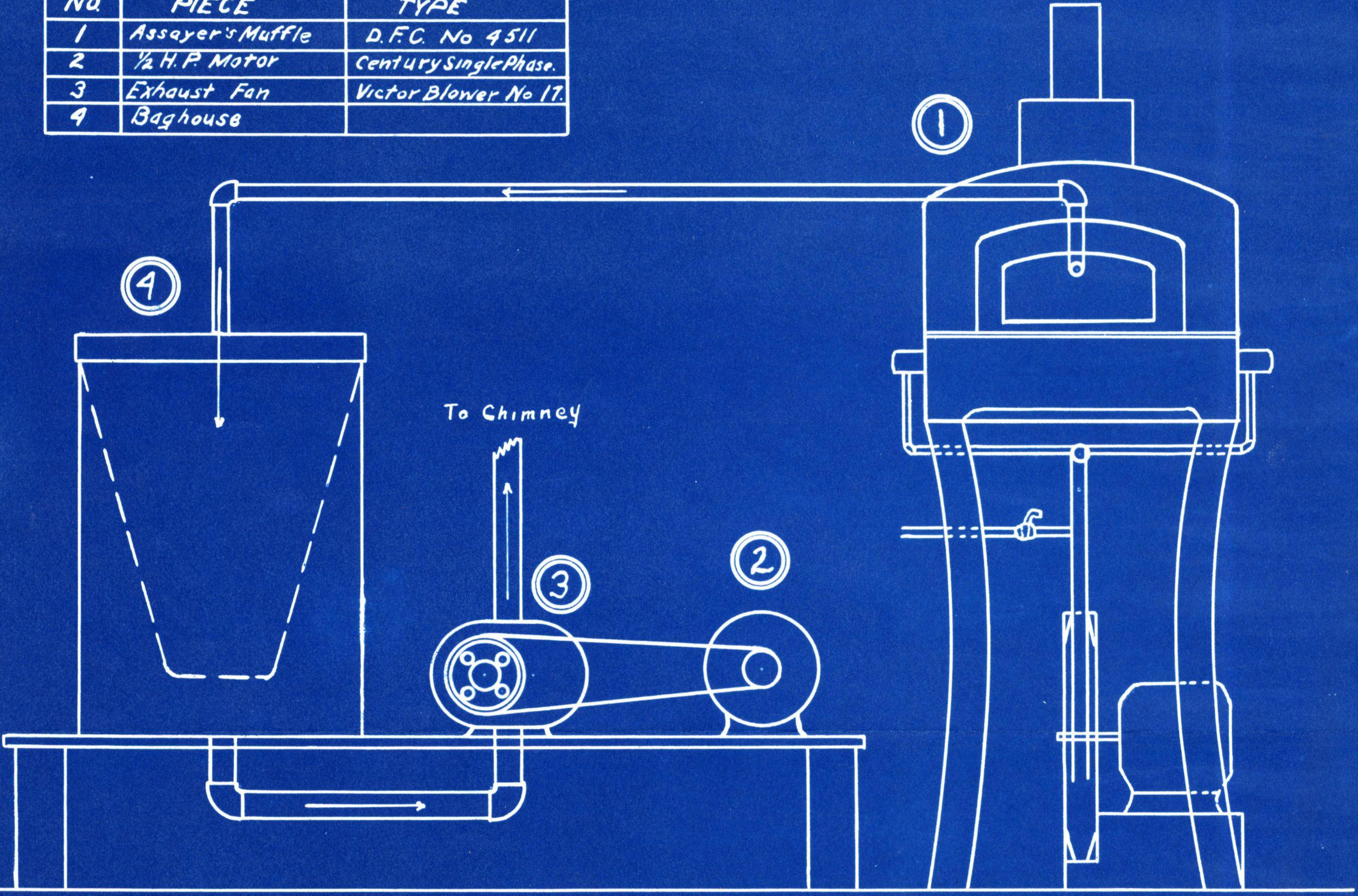

Figure 1.

length of time, and without the necessary handling to remove the fume, sould have lasted much longer. The bags after six or more runs became almost rigid, and opening them to remove the fume cracked open spaces in the sides and bottom, making necessary repairs, and ultimately a new bag became a necessity. Three bags were used during the entire series of determinations.

The baghouse was exhausted by the blower, capable of handling 1000 cubic feet of air per minute, but speeded down to one-third of this capacity. The gases, after passing thru the relatively large baghouse were quite cool--not over 40°C at any time--and for this reason did not seriously attack the interior. After a few runs, the exhaust fans were coated over with fume and oil, from the frequent oiling of the blower. From the bolwer, the gases were conducted thru a 2 inch pipe to the stack.

After charging the ore into the muffle, the furnace, heated by natural gas, was ignited, and the ore charge heated to the approximate temperature pre-arranged for that particular determination, or until the first fume made its appearance above the bed of the ore. The exhauster fan was then started, and the time recorded in the experiments taken as zero at this point. The mass was regularily rabbled at 5-minute intervals with a hoe-shaped rabble, care being taken that the calcine was of as constant composition as possible, and no 'dead' portions present.

Temperatures were measured to 1100°C by a standard Chromel P-Alumel thermocouple, as manufactured by the Hoskins Company of Detroit. The results were recorded by a Leeds-Northrup potentiometer-indicator. The thermocouple wires were protected from the highly acid gas by a fused silica tube. The potentiometer was standardized against the boiling-point of sulphur, calculated as 433.8°C from formulas to correct for barometric pressure,(1) and against the melting-point of silver, given as 955°C.(2)

Temperatures above 1100°C were determined by an optical pyrometer, manufactured by the Leeds-Northrup Co. of Philadelphia, the current being determined by a Weston milliammeter. The instrument had been standardized by the United States Bureau of Standards.

The run was continued, as a usual proceedure, with constant rabbling, until the fuming became almost negligible. Usually, fuming reached its maximum about 1.5 hours after the determination was commenced, and declined, until at about 3.5 hours it had apparently ceased. The time of the runs were extended beyond this due to sulphur elimination.

After the run was completed, the baghouse was opened, and the fume carefully removed with a fine brush. The pipes also were carefully brushed out, as a considerable amount of fume was deposited in them. The fume from both were carefully screened, to remove foreign matter, mixed, and thoroughly rolled, weighed, and sampled.

The muffle and calcine were allowed to cool over-night, the calcine removed, and the last part scraped out (as a considerable amount adhered rather firmly to the walls of the muffle), and weighed. The calcine was reduced to -20 mesh, rolled, and sampled. The sample was then reduced to -100 mesh and rolled.

For the development of the apparatus and method of proceedure,

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(1) International Critical Tables, Loc. Cit. v.3 p 247-8.

(2) Van Nostrand's Chemical Annual, 6th Edit, p 274. Van Nostrand Co. N.Y. 1926.

I am partly indebted to Mr. F.G. Bacon of the Midvale Plant of the United States Smelting and Refining Company.

For Test 8, a 750-gram graphite crucible was used. The calcine was placed in this, and loosely covered with a scorifying dish, having a hole in its center, which allowed the fumes to escape. This was placed in a ceramic pot furnace, and heated for the usual time, the temperature being determined by reading the temperature with the pyrometer, sighting thru the hole in the cover.

For Test 21, a special apparatus was utilized, as sketched in Figure 2. The gas, a mixture of 5% commercial carbon dioxide, and 95% of carbon monoxide, was stored in 45-liter carboys, and the gas gradually forced thru the furnace from the carboys by water displacement.

A constant pressure was secured by siphoning the water from a container into the bottom of the carboy; this pressure was kept at about one-half inch of water, measuring the pressure drop across the charge of ore.

The carbon monoxide was prepared from the action of sulphuric acid upon formic acid at about 100°C:

$$HCOOH + H_2SO_4 = H_2SO_4.H_2O + CO.$$

according to directions from Mellor.[10]

The charging, or reaction chamber was built by Mr. C.O. Ohrn. As noted in Figure 2, a 4 inch pipe was flattened to the dimensions, 3.25" x 5.5", and built according to specifications in Figure 2. This chamber fitted snugly into a small electric assayer's muffle,

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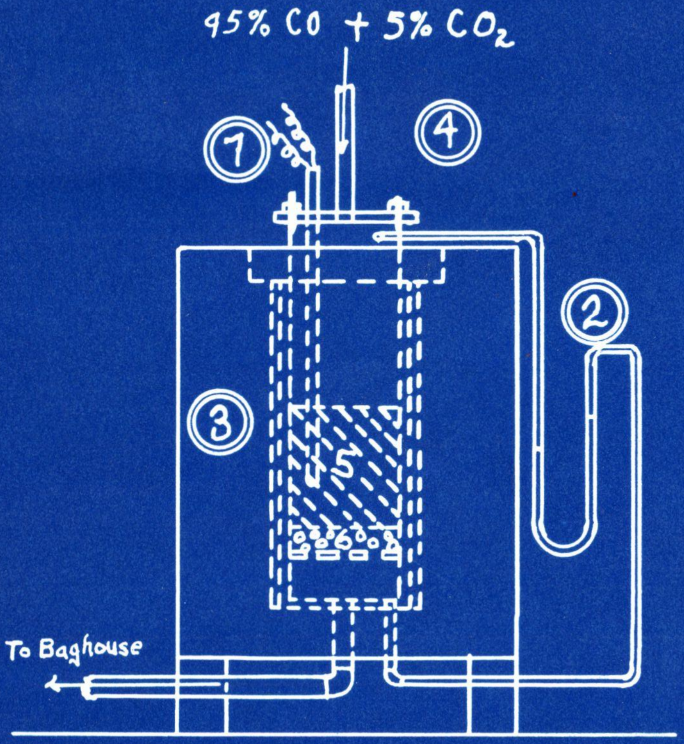
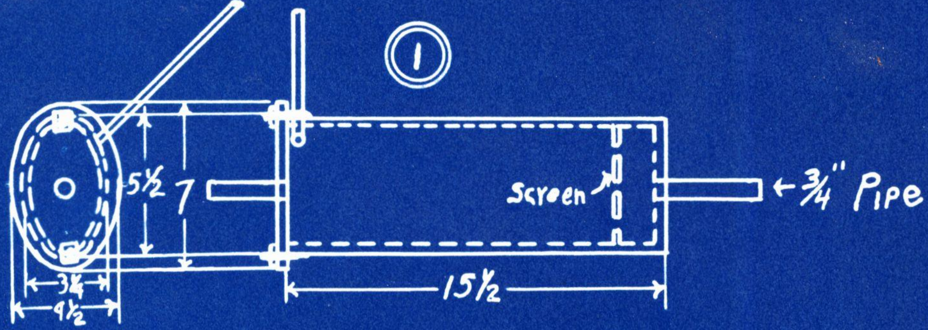
[10] Mellor, Loc. Cit. v.5 p 911. Longman & Co. London, 1924. 1st Edit.





NO.	PIECE	REMARKS
1	Detail Charging Chamber	Madefrom 4" pipe flatened
2	Water Manometer	To measure pressure drop
3	Muffle Furnace	Electric, replacable units
4	Charging Chamber	In place
5	Ore Charge	
6	Coarse Quartz	To hold fine ore up
7	Thermocouple	Chromel P-Alumel

Figure 2.

provided with a rheostat to regulate the current, and thus the heat. A special exit for the exhaust pipe was drilled in the back of the muffle. The muffle was turned with the door upward, supported on bricks, and the reaction chamber inserted. A layer of plus 10 mesh quartz was placed over the screen for the depth of one-half inch, 1500 grams of the calcine (-28 mesh) placed on the top of this, the lid tightly clamped on, and the system finally made gas-proof by luting with fire-clay.

The mass was heated to the desired temperature, the gases turned into the furnace, and the determination commenced. The pressure drop across the calcine was one-half inch of water, as measured by the water manometer. The gases from the reaction chamber were led thru a baghouse, similar to that sketched in Figure 1, but 14 inches in diameter and 28 inches tall. A cotton bag was used to catch the fume. After passing thru this bag, the exhaust fumes were carefully conveyed to a chimney by means of a .75 inch pipe.

Experimental Work.

A. Subdivisions of the Experiment.

As shown above, several possibilities present themselves upon which to develop methods whereby the volatilization of lead and cadmium from zinc concentrates or ores can be brought about. They are:

(1) The combination of the volatilization process with the necessary roasting of the zinc sulphides to the oxides, preliminary to reduction to the metal by either the retort or the electrolytic process. Paramount in importance in this method is the elimination of sulphur, but coupled to this may be the solution of the problem by utilizing the quantities of heat liberated during the process, or extraneous heat supplied, to raise the vapor pressures of the lead and cadmium oxides and sulphides to a point where true volatilization, as defined on page 10 may take place.

(2) The second possibility is the roasting of the zinc concentrates to the oxides, either with or without volatilization of a portion of the lead and cadmium by methods described under (1) above, and subsequently treating the oxides with reducing agents, coke, carbon monoxide, or the raw sulphide ore, in an attempt to further eliminate the impurities, especially cadmium, by reducing it to the metallic state, and boiling it off. Too, the boiling-point of cadmium is 776°C,(1) while that of lead is much higher---1525°C,(2) so it might be feasible to separate the lead and cadmium by this method. The theories of reduction have been discussed on page 20.

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(1) Van Nostrand's Chemical Annual, Loc.Cit. p 198.

(2) Ibid, p 228.

(3) The third possibility tried, was roasting a mixture of the sulphide ore with coke. While the literature gave no strong backing to this, as can be seen on page 22, during the preliminary determinations, it was found that cadmium in the fume from a roast of this kind was unexpectedly high, so a series of tests were made with this as a background.

B. Aims of the Experiment.

Summarizing, the aims of the experiment were:

(1) Complete elimination, as far as feasible, of all the sulphur from the ore, and a study of the final forms in which the sulphur remains in the calcine.

(2) A maximum recovery of the zinc in the calcine, as the oxide, and a study of the compounds formed during the roasting.

(3) A maximum volatilization of the cadmium from the calcine, and a maximum recovery of the metal in the fume. Also a study of the forms in which the cadmium remained in the calcine, and the form in which it was volatilized and collected.

(4) A maximum volatilization and collection of lead as fume, as incidental to the volatilization of the cadmium. This phase of the question has already been taken up by G.L. Oldright, who has definitely proven the proceedure of commercial value.(1) Mr. Oldright suggested this experiment in a letter to Mr. A.C. Fieldner, also of the U.S. Bureau of Mines, during 1920, as a continuation of his work upon the volatilization of lead from zinc. The problem, of course, at once resolves itself into the special study of cadmium, and the heat effects upon its compounds.

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(1) Oldright, G.L. Lead-Zinc Separation by Volatilization. Reports of Investigation #2544, U.S. Bureau of Mines. 1923.

Between Mr. Oldright's work and this experiment, there exists a fundamental difference in that his experiments were conducted upon concentrates of much higher lead content than those with which I contended. Oldright also states that the temperatures he records is probably considerably low,(1) a conclusion in keeping with my own experiences.

(5) A determination of the possibilities of separation of lead and cadmium within the fume itself, or during the volatilization by application of different measures for preferential volatilization of one.

C. Oxidizing Roasting Tests.

We have seen that a marked difference existed in the vapor pressures of the oxides of lead and cadmium from those of zinc between 1000° and 1300°C (Graph I). Thus, it should be possible to volatilize both the oxides of lead and cadmium, without even appreciable volatilization of zinc oxide between these temperatures, provided the lead and cadmium sulphides were first roasted to the oxides; that the calcine did not fuse or sinter, so that the area open to volatilization is not so low as to preclude commercial possibilities; or that chemical reaction with other ingreedients in the calcine prevented the volatilization of the oxides.

As to the possibility of chemical reaction, this is very slight. The formation of silicates would be the one most likely to occur, due to the low fusion points of these compounds, especially the lead silicates.(2) However, the concentrates ran very low in silica, 2-3%, as can be seen in Table I; also the liklihood of the zinc making the reaction is very high,

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(1) Oldright, Loc. Cit. p 7.

(2) Ibid, p 3.

due to the large excess of this oxide, and the application of the law of mass action. Too, the oxides of lead tend to volatilize as soon as they are formed, especially if there is a rapid circulation of gas.(1) This same can be assumed true of the cadmium products.

The agglomerating stage was reached on each different concentrate at 1150-1200°C, but true fusion began at about 1250-1300°C; this was noted in only Test 8. To secure the maximum volatilization, the mass should not be sintered, as the mass occludes large quantities of the material that would otherwise be volatilized. Hence, it would seem that the practical limits are 1000 to 1200°C.

Other factors also begin to enter into commercial possibilities when we go above 1200°C. The first of these is holding the temperature for any length of time involves the expenditure of large amounts of fuel. Radiation and conduction losses begin to be a predominant factor. We also have the question of providing suitable equipment to withstand the very high temperatures, and the avidity of all substances for slagging at these temperatures is well known.

Oldright shows that the volatilization of PbO begins at 600, and reaches a maximum at 950°C.(2) For the triple purpose of determining the point best suited for the roasting of the concentrates, for the lower points on the oxide volatilization curve of lead oxide and cadmium oxide, and most important, to demonstrate the possibility of separation of lead oxide and cadmium oxide between 700 and 1000°C (Assuming the vapor pressure curves of lead oxide in Graph I as too low, and Oldright's results as correct), three determinations were made. The complete data upon these

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(1) Oldright, Loc. Cit. p 4.

(2) Ibid, p 6.

determinations are included under Tests 1, 2, and 3, Tables III, IV, V, and VI.

Test 1: Charge, 6000 grams of "D", Table I. Temperature kept at 700 ± 25°C for 6 hours. This calcine was sampled once each hour, to determine the sulphide sulphur in the calcine. Weight of calcine, 5343 grams. Weight of fume, 34.5 grams. For complete data, see Test 1, Tables III, IV, V, VI, and XVI.

Test 2: Charge, 6000 grams of "D", Table I. Kept at 800 ± 20°C for 5 hours, 30 minutes. Calcine sampled hourly. Weight of calcine, 5297 grams; weight of fume, 32.5 grams.

Test 3: Charge, 6000 grams of "B", Table I. Kept at 900°C for 5 hours, 40 minutes, with considerable variations in temperature. Weight of calcine, 4855 grams; weight of fume, 93.5 grams.

As can be seen in Table XVI below, the attempted separation of lead and cadmium by this method was fruitless, and this is even better brought out by Graph III.

We have therefore definitely proven the fruitlessness of any attempts at either the volatilization of, or separation of, lead and cadmium minerals up to 900°C, by volatilization.

Therefore, we turn our attentions to still higher temperatures, haven proven that the vapor pressures of lead and cadmium oxides are too low for definite volatilization up to 900°C. The following series of oxidizing roasts were carried out, for further development of the theory of oxide volatilization.

Test 4: Charge, 6000 grams of "B" sample, Table I. Average temperature, 985 ± 25°C for 4 hours, 20 minutes. The temperature

Table XVI.

Temperature Effects of upon the volatilization of lead, cadmium and zinc ~~oxides~~ from zinc concentrates ~~thru~~ on heating in an oxidizing atmosphere roasting.

Temperature °C	Time hours	Percentage of original Element in Calcine			Percentage of original Element in fume.			State Fusion of Calcine
		Zn	Pb	Cd	Zn	Pb	Cd	
700°C	6.0	98.7	90.0	92.6	.25	.99	1.05	none
800	5.5	93.7	90.8	95.5	.31	.91	.49	"
900	5.66	91.3	80.7	68.1	1.34	2.75	1.40	"
985	4.33	91.4	52.8	93.4	1.12	11.95	8.33	"
1050	4.50	91.4	60.5	67.2	1.00	23.5	11.25	"
1100	4.00	94.8	36.4	51.1	1.12	36.5	20.25	slight but porous
1190	4.25	87.6	18.5	40.3	1.09	40.4	26.4	badly nodulized
1320	5.00	97.8	6.33	5.9	not	caught,	→	semi-fluid

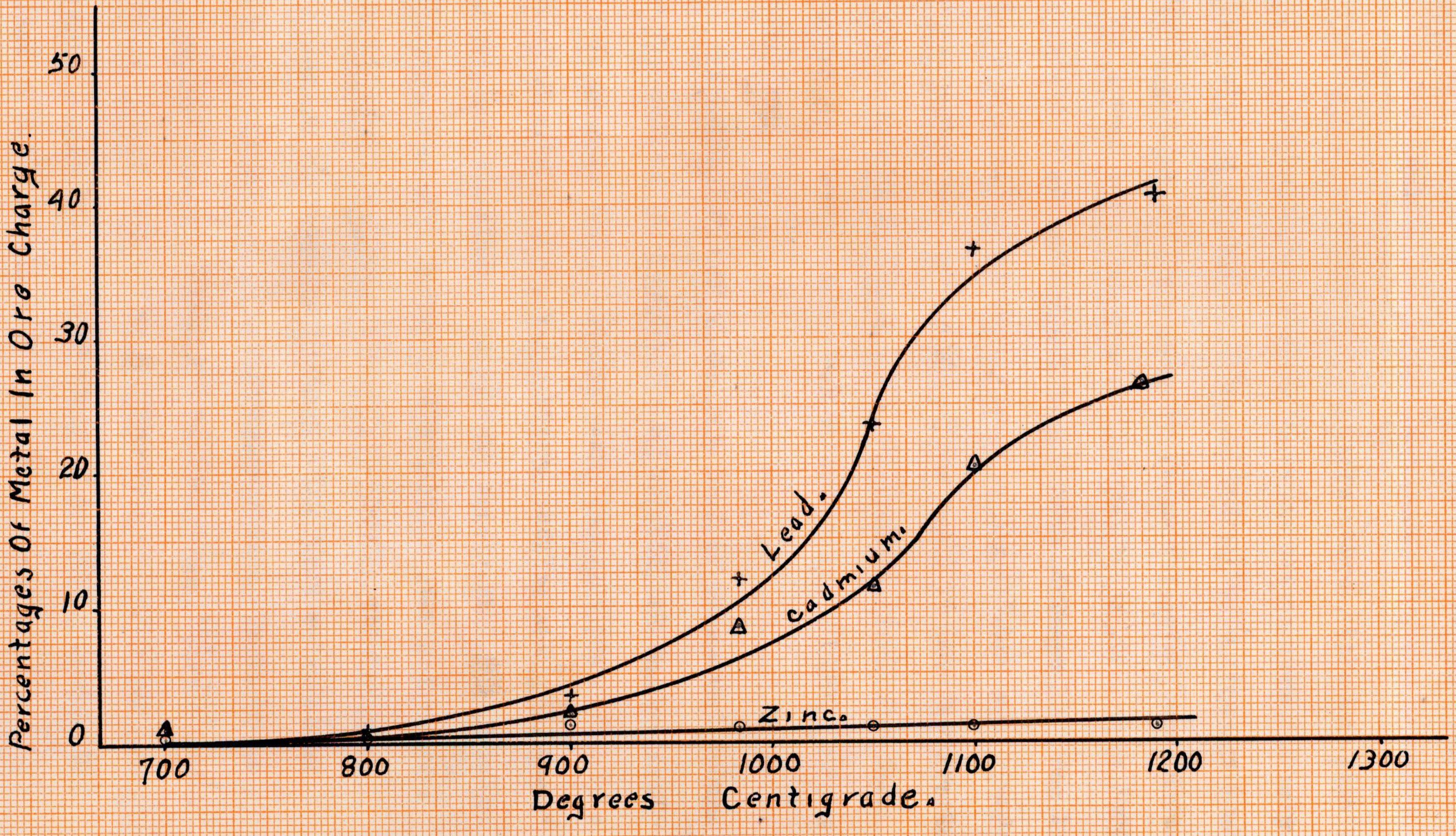
mentioned above is approximately the point where the vapor pressures of cadmium and lead oxides become marked on Graph I. Weight of calcine, 4855 grams; weight of fume, 119.5 grams. For total data, see Test 4, Tables III, IV, V, VI. As can be seen in Graph III, or Table XVI, both the lead and cadmium are being volatilized to a noticeable extent, while the percentages of each of these elements, in the calcine, are beginning to show a decided drop. Graph II.

Test 5: Charge, 6000 grams of "B", Table I. Average temperature, 1050°C; time of run, 4 hours, 30 minutes. The collection of both lead and cadmium in the fume is beginning to assume commercial possibilities, while the fall in the calcine percentages (see Graph II) is still strong, indicating the trial of still higher temperatures. See also Tables III, IV, V, and VI, Test 5.

Test 6: Charge, 6000 grams of "B", Table I. Average temperature, 1100°C; time of run, 4 hours. As yet the calcine remained largely a loose, porus mass, with very little sintering, indicating that the formation of lead slags with the silica had not occurred. The calcine curves (Graph II) still show the steady drop, while those of the volatilization products mounts (Graph III) appreciably. All indications are toward the use of still higher temperatures.

Test 7: Charge, 6000 grams of "B", Table I. Average temperature, 1190 - 35°C, time of run, 4 hours, 15 minutes. This was the average maximum temperature attainable with the apparatus sketched in Figure 1. The calcine was badly sintered, and nodulation or agglomeration was very apparent. However, the calcine curves still drop steadily, but the collection rate shows some tendency to drop off, both as to the lead and cadmium. For analysis, see Tables III, IV, V, and VI. Encouraged by the fall of the calcine percentages, we pass to Test 8.

Test 8: As we desired to test still higher temperatures, and the limit of the original apparatus had been reached in Test 7, we determined to try the effects of roasting in the graphite crucible described on page 43. As this was intended to be the highest temperature tested, it was decided to use calcine from Test 1, knowing that the cadmium and lead were still present in representative quantities, and thus save the possible trouble of the sulphides fusing or otherwise misbehaving below the maximum temperature. 500 grams of this calcine was placed in the crucible, and treated for 5 hours at an average temperature of 1320°C. No fume collection was made, or even feasible with the apparatus used. The calcine assumed a semi-fluid state of fusion; at the end of the test,



Graph III. Pb, Cd and Zn Volatilized and Collected.

the fusion was complete. Analysis of the resulting calcine gave the last points on Graph II. Weight of calcine, 420 grams. We find that volatilization is well-nigh complete at this temperature, while but little of the zinc is lost. Seemingly, zinc oxide vaporization is approximately as low as that indicated by Graph I at 1300, for very little zinc was lost.

Intrepeting the results obtained, the following facts loom large: (1) The higher the temperature, the greater the volatilization, with 100% volatilization possible of accomplishment in 4-5 hours between 1300 and 1350°C. (2) The exceedingly apparent relationship between the volatilization curves and the vapor pressure curves of the oxide of the metal at that temperarture, as comparisons between Graphs I, II, and III will reveal. (3) The fact that lead and cadmium are inappreciably volatilized under 1000°C, in this series of determinations.

Taking a slightly different viewpoint, that of commercial value, my impression of the work is the feasibility of volatilization at approximately 1100°C, with no sintering of the calcine, and as discussed later, the nice sulphur elimination at this temperature, coupled with what would seem to indicate complete volatilization of both metals from the calcine in from 15 to 20 hours, assuming the rate of volatilization a constant.

It is surprising, no doubt, that little zinc is volatilized during the whole process, as revealed by Graph III. That volatilized is beyond a shadow of a doubt due to mechanical dusting. It is to be remembered that the ore used was floatation concentrates, 95% -100 mesh, and a fair percentage finer than 200 mesh. The frequent rabbling would account for the zinc volatilized; a comparison of the zinc, lead, and cadmium volatilized at 800°C (Table XVI) shows that these are almost a constant. The recovery of the zinc in the calcine was very uniform, also, and gives no rise to the question as to whether we need worry about the volatilization of zinc oxide below 1300°C. The percentages lost are due to other causes--as sampling of calcine at intervals; some adsorption of zinc into the muffle walls (always a noticeable factor in the retorting of zinc, about 1.2% at one American plant)(1). The average recovery is as good or better than good retorting practice, altho the temperatures is approximately the same. However, little volatilization of zinc is to be expected from Graph I. One major point was accomplished--the maximum zinc was retained in the calcine throughout this series of tests. (Graph II).

Viewing the percentage of lead and cadmium volatilized and collected in Graph III, we at once realize that at any one temperature, a definite relationship exists between the total lead and the total cadmium percentages collected in the fume. In fact, the relationship is very simple:

$$.588\ X = Y$$

Where X is the percentage of lead volatilized and collected, and Y the percentage of cadmium volatilized and collected. This is obtained by averaging the data obtained from 900° to 1190°, Table XVI. This relationship holds with but inappreciable error over the whole range. The graph obtained for this volatilization-collection range does not follow the vapor pressure curve (Graph I) very exactly, but it is to be realized that it is very flexible, due to the efficiency of the baghouse, apparently in the neighborhood of 60%, judging from the percentage of the metals thrown out of the calcine to the percentage found in the fume.

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(1) Ingalls, Loc. Cit. p 540-41.

Howeverm this factor was one hard to manage at the best.

Viewing the relationship of the lead to the cadmium in the calcine, it would seem that the percentage of cadmium volatilized runs in the neighborhood of 15% less than that of the lead--which is to be expected from Graph I, since the cadmium oxide curve is almost the lead curve less a constant factor. The relationxhip between Graphs I and II shows very well that the lead and cadmium are volatilized from the calcine as the oxides, a statement later verified as to cadmium.

Another, and the major object of this series of experiments was the complete elimination of the sulphur, as far as possible. Toward this objective, a study was made of the percentage of sulphide and sulphate sulphur in the calcines during the progress of the roasts, both in the above series, and in the roasts preliminary to the later work in reduction and volatilization of the cadmium.

Mellor(1) reports that the best temperature for roasting zinc blende is about 960°C, a statement in which I am in accord. The results given below (Table XVII) were ascertained by thoroughly mixing the calcine, in the muffle, with the rabble, and then taking a "grab" sample, cooling quickly, and determining the sulphate and total sulphur, from which the sulphide sulphur was determined by difference. Table XVII below shows the results at different temperatures for the oxidizing roasts, as determined from Tests 1, 2, 11, 12 and 16.

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(1) Mellor, Loc. Cit. v.4 p 602.

Table XVII.

Rate of Sulphide Sulphur Elimination from Calcine.

Time	Sulphide Sulphur content of the calcine at different periods of roast at the several temperatures:				
	700°C	800°C	950°C	975°C	1100°C
Beginning	27.69	26.47	—	27.9	24.53
:30			21.29	24.74	20.79
1:00	19.27	24.50	17.81	18.55	18.51
1:30			13.64	16.75	17.65
1:45	17.35				
2:00		12.63	10.08	12.24	10.85
2:30			2.50	7.11	7.85
2:45		10.22			
3:00	10.81			5.60	4.20
3:10			1.46		
3:30				.52	.51
3:50		4.54			
4:00	4.11		.00	.14	.05
5:00	2.31	.25			
5:35		.09			
6:00	.10				

The results given in the above table are plotted in Graph IV. From this graph, it is readily seen that the rate of elimination of sulphur is fastest in the neighborhood of 950°C, and that this rate of elimination is uniformly a straight line until the calcine is reduced to less than 1% of sulphide sulphur. This is reduced to the theoretically perfect roast, as Hofman sees it.(1)

As stated above, the rate of sulphur elimination is a straight line graph, hence it should fit into a straight-line formula. Such, indeed, is the case. Using the two-point form of the equation of the straight line,(2)

$$\frac{Y - y'}{y'' - y'} = \frac{X - x'}{x'' - x'} \quad (1)$$

If X is taken as the percentage of sulphur present, and Y the time in hours, substituting the data from 1.0 hours and 2.00 hours in the above table, we have the equation:

$$X = 25.5 - 7.7\,Y \quad (2).$$

But this form is for a particular case. Letting C represent the original percentage of sulphur (a constant), and X, the percentage of sulphide sulphur left in the calcine after a given number of hours, Y, we have:

$$X = C - 7.5\,Y \quad (3)$$

with little error. By solving for Y = 0 in (2), we have the probable original composition of the ore at the beginning of the determination, which would correspond to C in equation (3). Assuming (3) to be correct, it is therefore theoretically possible to eliminate all of the sulphur in a 30% zinc sulphide ore in 4.5 hours from the time of ignition of the sulphide, when the average temperature of the roast is 950°C. It was due to this consideration that all roasts were carried out for 4 to 4.5 hours, after it was discovered in Test 4 and Test 5 (it being understood that, as revealed by the figures in Table XVII, the sulphur was

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(1) Hofman, Loc. Cit. p 73.

(2) Handbook of Chemistry and Physics, Loc. Cit. p 20.

reduced below 30% by heating to the temperature in question, when the time was recorded as zero hours.) As stated on page 42, the lessening of the fuming at about this period of time was also taken into consideration as a criterion of the completion of the test.

One question might be raised here, will this equation hold from the beginning of the roast? Yes, if the ore is heated to the temperature at a rate as fast as possible. It takes about one hour to raise the calcine from room temperature to 950°C, and the average composition was about 32% sulphur. As the solution of the above equation (2) shows, at the beginning of the determination (after one hour of preheating) the composition of the calcine was approximately 25% sulphur--about the 7.5% hourly elimination indicated by the equation.

One other question of interest is the form in which the zinc remains in the calcine. Prominent among the compounds of interest during the reduction process is the formation of zinc ferrites, which is due to the intimate contact of the oxides of iron and zinc, in which the reaction:

$$ZnO + Fe_2O_3 = ZnFe_2O_4,^{(1),(2)}$$

which begins at about 650°C.

Considerable work has been done upon this compound at the Utah Engineering Experiment Station by Oldright, Niconoff, and Hultgren. Their results tend to show that the composition is constant up to 950°C, but have not extended their results beyond this temperature.

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(1) Hofman, Loc. Cit. p 44.

(2) Ingalls, Loc. Cit. p 32.

As the ferrites are a source of loss both in the electrolytic process, due to their relative insolubility in dilute sulphuric acid,(2) and their comparative difficulty of reduction in the zinc retorting process,(3) for this reason it would be well to find out just what effect the very high temperatures used in these experiments had upon the formation of ferrites. The analysis upon the dead-roasted product was conducted by leaching 2 hours, with constant agitation, a sample of the calcine in Low's Solution, at 37°C, by methods devised by W.F. Keck and others of the Utah Engineering Experiment Station, but as yet unpublished.(1)

Dice 2 hr at 40°c

The formula, $ZnFe_2O_4$ (or $ZnO.Fe_2O_3$) calls for 1 gram of zinc to each 1.71 grams of iron held insoluble. The results in Table XVIII were obtained upon testing for zinc ferrites in high temperature calcines.

Table XVIII.

Composition of Zinc Ferrites, 900°-1200°C.

Temp.	Percent Insoluble Zinc	Percent Insol. Fe	Ratio Zn : Fe
900°C	3.68	6.1	1 : 1.66
965	5.35	7.0	1 : 1.31
1050	5.25	6.4	1 : 1.22
1100	5.37	6.9	1 : 1.29
1190	5.22	7.68	1 : 1.49

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(1) Method to be published.

(2) Liddell, Loc. Cit. p 1102.

(3) Bray, Loc. Cit. p 277.

Viewing the above results, it seems that considerably more than the theoretical amount of zinc is held insoluble; however, at 900°C, the correspondence to the formula is very good. In fact, the first tends to show that the formula, $ZnFe_2O_4$ holds to about 950°C, and then the results tend to lend support to Hofman's statement that $2ZnO.Fe_2O_3$ and compounds higher in zinc are formed.(1)

The formation of ferrites is, indeed, one of the most adverse factors in the final solution of this problem; and it will probably be the predominent factor against the roasting at these advanced temperatures to secure maximum volatilization. Especially is this true with the electrolytic industry, should they decide to adopt volatilization, as the ferrites demand a long and costly proceedure of treatment.(2)

As to the forms in which the cadmium occurs in both the fume and the calcine, you are referred to pages 77 to 80, this thesis.

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(1) Hofman, Loc. Cit. p 44.

2) Tainton, U.C. Loc. Cit. Eng. & Min. Jour. v. 126, p 856. 1928.

D. Reducing Tests Upon Oxidized Samples.

As stated at the beginning of the experimental work, this division is subdivided into three main classes: (1) Treatment with coke, (2) Treatment with carbon monoxide, and (3) Treatment with the raw sulphide ore. While each of these was prompted by a different motive, the general aim was the same--depending upon the reduction of both cadmium and lead oxides to the metallic state, and boiling off the cadmium, but not the lead. The general purpose of course was to secure the maximum volatilization of the cadmium, with little or no attention being paid to the lead, this already having been taken care of by the oxidizing roasts discussed in division C.

Preliminary to each run, the ore was calcined for a time calculated from the figures given in Table XVII--4 hours. From Graph IV it can be seen that the opportune temperatures for roasting the ore are between 950 and 1100°C, and these two temperatures were adopted as the preliminary treatment for this series of determinations.

1. Tests with Coke.

This series of runs was prompted by the roasting practice of adding coal to the last one or two hearths of the Wedge furnaces used in the roasting of zinc ores. Primarily, the reason for the addition of coke is to maintain the highest temperatures at the end of the roast, but the possibility of reducing and so volatilizing some of the impurities is easily seen. Adhering to the idea of the Wedge roaster, which the apparatus more or less resembles, a series of tests were made at various temperatures upon previously calcined (4 hours at 950-975°C) body of ore, adding a definite amount of coke (500 grams) while the ore was still at this temperature, and the roast continued at the temperature until the fume produced by the coke slackened.

While it was realized that the coke would exert a reducing action upon the zinc, it was hoped that it would also attack the cadmium, which, according to Hofman, is reduced from 702 to 813°C, while zinc is reduced from 1022 to 1068°C.(1)

Such, indeed, proved the case. While considerable zinc was reduced below 1100°C (the zinc distillation usually began around 1060°C) the quantity of the cadmium in the fume grew greatly to that in the calcine. Actually, a concentration up to 10 to 1 was effected as far as the cadmium content of the fume was concerned, when compared with the original ore. With it, however, was volatilized up to 16% of the zinc. The following table gives the maximum recoveries, in actual assay percentage of the element present in the fume and calcine, and the corresponding volatilization of the zinc:

Table XIX.

Comparison of Cadmium Enrichment of Fume, and Zinc Volatilized.

Temp.	Percent Cd Heads. :	Percent Cd, Reducing : fume	Percent of total zinc volatilized.
1000°C	.51	2.28	3.61
1100	.35	3.61	1.10
1200	.35	3.98	2.43

Note: Columns 2 and 3 assay values; Column 4, zinc present is 100%.

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(1) Hofman, Loc. Cit. p 320.

Table XIX gives the results obtained in their most favorable light; however, the action of the coke was too uncertain for steady recoveries such as these.

During a portion of these runs, the oxidizing fume was kept separate from the reducing fume; however, in the final five (in point of time of determination) the oxidizing and reducing fume was caught in the same bag, since it was assumed that previous tests were conclusive enough to demonstrate that the amount of cadmium volatilized up to 950°C was about a constant, .5 grams of cadmium, carrying also 3.6 grams of lead, as a study of the following figures will show (Taken from Tables IV).

Table XX.

Grams of lead and Cadmium Volatilized at 950°C:

	Gm. Cd.	Gm. Pb.
Test 3	.16	5.3
Test 12	.7	3.7
Test 13	.5	2.0
Test 15	.6	3.4
Average	.5	3.6

Hereafter, therefore, use was made of this fact, and the cadmium and lead of both the oxidizing and reducing fume caught together.

With the background discussed above, trials were begun:

Test 9: Utilizing 6000 grams of the "C" Sample, Table I, roasting for 4 hours at 975°C, adding 500 grams of coke, thoroughly mixing, and raising the temperature to 1000°C for 1.5 hours, the results embodied in Table XXI, Test 9 was obtained. See also Tables III, IV, V, and VI for complete analysis of this determination. This run was purely

~~Table XXI.~~

Data on Heating Oxidized Calcine with Coke

Resumé of ~~Coke and Oxide Tests, From Tables III, IV, and V.~~

6000 grms original ore given oxidizing Roast, then 500 grams of coke added.

6
3

	Temperature, °C		Time used for Roasting, hours		Per Cent of % Element caught in Fume			Percent of ~~%~~ Element Remaining in Calcine.		
Test	~~Temp.~~ oxidizing roast	~~Temp~~ Red. using Roast	~~Time~~ ox. oxidizing Roast	~~Time~~ Red. using Roast	Pb	Cd	Zn	Pb	Cd	Zn
9.	975	1000	4 Hr.	1.5 Hr	2.7	.5	.1	68.3	67.7	89.7
10.	975	1000	4	2.06	12.28	19.3	3.61	71.7	55.6	90.9
11.	975	1100	4	2.16	19.25	25.8	6.38	56.0	51.7	82.4
12.	975	1060	6	2.5	3.9	6.2	2.97	72.3	58.1	84.2
13.	9 950	1200	4.25	1.33	6.3	15.3	2.43	46.0	28.6	79.5
14.	975	1200	4.	3.66	20.2	19.5	7.76	49.7	33.3	77.7
15.	975 -3Hr 1100 -3Hr	1100	6	2.0	5.4	7.2	1.68	61.3	30.5	64.2
16.	1125	1100	3.83	1.33	13.5	6.7	1.1	49.8	54.3	87.8
17.	1100	1100	4.	1.5	31.7	22.4	6.13	47.9	32.9	84.3
18.	1100	1200	4	2.0	53.4	45.2	16.0	25.9	29.1	71.5

projective, attempting to locate points from which to begin another series of tests, and, if possible, to ascertain whether the experiment should be carried out at a higher or lower temperature. Too, it was hoped to reduce the all-too-high temperatures needed in the volatilization in the oxidizing roasts. While relatively one-third of both the cadmium and lead were volatilized (Table XXI) it was thought best to make another determination under the same conditions, except to let the reducing action go for a short time longer. Weight of Calcine, 5060 grams; weight of oxide fume, 17 grams; weight of reducing fume, 4 grams.

Test 10: This determination was carried out on 6000 grams of "D", Table I. The sulphur was eliminated in a 4-hour, 975°C roast, 500 grams of coke added, and the temperature raised to 1000°C and held there for 2 hours and 5 minutes. Weight of calcine, 5159 grams; weight of the mixed oxide-reducing fume, 258 grams. Reviewing Table XXI, it can be seen that 45% of the cadmium was volatilized from the calcine, while 91% of the zinc remained. The calcine figures in both Tests 9 and 10 for both the remaining percentage of lead and zinc in the calcine is surprisingly close. The greatest effect is upon the desired point--the cadmium. Indications were for higher temperatures, so Test 11 was made.

Test 11. Charge, 6000 grams of "D" Sample, Table I. Calcined at 975°C for 4 hours, then 500 grams of coke added, and the roast finished for two hours and 10 minutes at 1100°C. The results are somewhat better, but at the cost of considerably more zinc, as can be seen in Table XXI.

Test 12. Thinking to reduce the zinc volatilization revealed in Test 11, and also reduce the sulphur content of Test 11, a 6000 gram sample of "C", Table I was calcined for 6 hours at 975°C, then 500 grams of coke added, and the reducing roast carried on for 2.5 hours longer, at 1060°C. The results were dubious; in fact, the cadmium content of the calcine was higher than that of Test 10.

Test 13. It was then determined to try still higher temperatures on the reducing roasts. A 6000 gram sample of "C", Table I was calcined for 4.25 hours at 950°C, the customary 500 grams of coke added, and the temperatures raised to the maximum obtainable, 1200°C, and held there for 1.37 hours. The fuming was exceedingly profuse; however the cadmium content in the calcine dropped only 28%, but a loss of 20% of the zinc occured in the calcine. During the reducing roast, the bag became overheated, and was ruined, necessitating the repetition of the determination. One very promising factor developed--the cadmium content of the fume in the pipes was the highest recorded throughout the whole series of tests--4%. This suggested the possibility of collecting the cadmium in the pipes, and catching the lead in the bags, and in this way separate the two. Later attempts at this separation, however, proved to be futile.

Test 14. The same proceedure was followed as in Test 13, except that the reducing roast was prolonged for 3 hours and 40 minutes. However, results are comparable with those of Test 13 (See table XXI). Two-thirds of the cadmium was taken from the calcine at the expense of 22% of the zinc lost from the calcine. From this latter factor, therefore, it would appear that these advanced temperatures are commercially undesirable, and so I turned to other experiments.

Test 15. Realizing that perhaps Test 11 and Test 3 might present a possibility of eliminating the sulphur at 975°C, then removing the majority of the cadmium by straight oxidizing roasting for 3 hours at 1100°C, and finishing the cadmium elimination by the promising elimination at

1100°C with 500 grams of coke, this experiment was tried upon 6000 grams of "C" sample, Table I. See Table XXI for results. 70% of the cadmium was eliminated, at a cost of 35% of the zinc from the calcine. This tremendous zinc volatilization dictated immediate abandonment of this effort

Test 16. 6000 grams of "C" sample, Table I was oxidized for 3 hours, 50 minutes at 1125°C, followed by a reducing roast at 1100°C for one hour, 20 minutes. Forty-six percent of the cadmium was volatilized, and the lead percentage of the calcine cut to 46% of the original, so this determination gave another opening from which to start other work. 87% of the zinc remained in the calcine, one of the highest of all of this series of reducing roasts, so a check determination was made to find out why this was true.

Test 17: Checking Test 16, 6000 grams of "C" sample was calcined for 4 hours at 1100°C, followed by 1.5 hours of reducing roast at 1100°C, with 500 grams of coke as the reducing agent. Weight of calcine 4630 grams; weight of mixed fume, 444 grams. This determination shows that at a cost of 13% of the zinc to the calcine (rather a low loss, as compared to the losses in the oxidizing tests, 1 to 8), the cadmium in the calcine can be cut to 37% of its original, and a large portion caught in the baghouse. Encouraged by these results, it was determined to try the maximum reducing temperatures obtainable, although warned by previous tests that it would fail:

Test 18: Using 6000 grams of "I" sample, the charge was calcined for 4 hours at 1100°C, 500 grams of coke added, and the roast continued for two hours at 1200°C. Weight of calcine, 4003 grams; weight of fume, 942 grams. We have here almost a small-scale distillation plant for zinc; 16% of it was secured in the bag. As far as practical purposes are concerned, this determination was useless, although 29% of the cadmium alone remained in the calcine, and over 53% of the lead was volatilized and collected, along with 45% of the cadmium--both of these fume recoveries being very high.

Viewing the above series of determinations, one fact is very apparent--the action of the coke is far from uniform, and therefore we cannot rely to a great extent upon the results obtained thru its use.

Conclu

However, it seems that the cadmium can be volatilized down to approximately 30% of the original (in the calcine) by the use of coke at 1100°C for 2 hours, following an oxidizing roast at 1100°C for 4 hours. This is 20% more of the cadmium taken out of the calcine than was taken out in Test 6, so for this reason it would seem that it has some commercial possibilities. However, temperatures above 1100°C are disasterous, volatilizing from 7 to 16% of the zinc, and do not have a corresponding effect on the lead and cadmium.

The determinations at 1000°C hold the greatest commercial value, however. This temperature is not much above the temperatures used in commercial practice, and as Test 10 ably demonstrates, it would be a simple matter to add coke or coal to the last two hearths of the roaster, raise the temperature to 1000°C, and volatilize practically half of the cadmium off. Reducing roasts at this temperature, also, have a beneficial effect in breaking down zinc ferrites.

2. Tests Using Sulphide Ore as the Reducing Reagent.

In the smelting of lead ores, the reactions,(1)

$$PbS + PbSO_4 = 2\ Pb + 2\ SO_2$$

$$2\ PbO + PbS = 3\ Pb + SO_2$$

and if an oxidizing condition is maintained, the lead will react:

$$2\ Pb + O_2 = 2\ PbO$$

and the lead oxide volatilize as such, as under the oxidizing roasts of this series. As has already been emphasized, the lead would not boil off in the metallic state, as the boiling point is 1525°C, but the vapor pressure is great enough to allow rapid oxidation, and therefore sublimation of the oxide. This has already been discussed on Page 22.

The literature did not reveal any such reactions for the zinc, and upon cadmium undergoing this reaction, the literature was entirely silent, though intimating that the zinc reactions would not proceed.

At Mr. G.L. Oldright's suggestion that this reaction might be extended to cadmium, and should assist materially in the volatilization of the lead, two experiments were carried out, both in the nature of projective experiments.

Considering the fact that two parts of the oxide react with one part of the sulphide (by molecular weights) in the above lead equations, the procedure was decided upon: 4000 grams of the sulphide ore was calcined for 5 hours, 15 minutes at 950°C. This was allowed to cool, and then thoroughly mixed with 2000 grams of the raw sulphide ore. It is

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(1) Bray. Loc. Cit. p 214.

readily seen that the oxidation process simply placed the oxides in the proper ratio for the sulphides, without complicated chemical maneuvers to convert one to the other. With the mixture as above, the determinations were made:

Test 19: The migture described was of the "D" sample, Table I. It was heated to 1100°C, and kept at this temperature for five hours. The mass fumed well for the first 3.5 hours, then the fuming gradually died away at the end. The collected fume weighed 93 grams; the calcine 5115 grams. A very low net recovery of the cadmium is recorded for this determination (Table IV) though the cadmium was reduced to 53.8% in the calcine, which is very nearly identical with the 51.1% cadmium in Test 6, so it must be concluded for this run that any cadmium expelled is due only to the oxidizing roast, and not to any effect due to the addition of the raw sulphide ore. The lead, on the other hand, was adversly effected, when the comparisons between Test 6 and this test is made. In the former test, only 26.4% of the lead remained in the calcine, while here 66.2% remained, doubtless due to the lead reactions given above. It must therefore be concluded that the run gave negative results, see Table XXII.

Table XXII.

Effect of Sulphide-Oxide Reducing Roasts on Zn, Pb, and Cd.

Test	Percent of element in the fume			Percent of Element in Calcine		
	Pb	Cd	Zn	Pb	Cd	Zn
19	9.18	3.9	.42	66.2	53.8	93.2
20	43.0	17.3	10.0	Trace.	8.2	57.0

Test 20. Although Test 19 had turned out adversly, it was decided to try one roast on the series at 1200°C. The same mixture, one-third raw sulphide ore, two-thirds calcine from Sample "D", Table I, was heated to 1200°C, and maintained at this temperature for 4 hours. The fuming was very profuse during the determination, and the calcine reached a highly plastic stage, becoming rock-like when cold. This was undoubtedly due to the sulphide of zinc melting, or fusing, at about 1160. Fumes escaped plentifully, indicating a very rapid reduction, and perhaps boiling of the calcine in the furnace. A very poor calcine recovery was recorded--3125 grams; 432 grams of fume was collected in the baghouse, and 212 grams in the pipes. Undoubtedly a portion of the fume was due to the volatilization of ZnS, which burned to the oxide before deposition.

The test at 1100°C shows no possibilities at all--that at 1200°C, the mass became almost fluid, and while all of the lead and a great majority of the cadmium was volatilized, the mere fact that the calcine became fluid dictates an abandonment of this idea in any normal roasting practice.

My conclusions from this series of determinations is therefore that the reaction hoped to develop is obscured by more adverse factors than advantages, viewed from a commercial light. The probability is that the cadmium, being almost a chemical twin of zinc, does not follow the lead reaction in the least. This series of determinations, for that reason, has therefore proven unfruitful.

3. The Carbon Monoxide-Oxide Test:

As mentioned above, one test was carried out using carbon monoxide as the reducing agent. Mr. C.G. Maier of the Berkeley Station of the United States Bureau of Mines kindly calculated that the carbon monoxide-carbon dioxide for equilibria with zinc and with cadmium over a considerable temperature range, and found that 95% carbon monoxide and 5% carbon dioxide gas would be strongly reducing to cadmium oxide between 750 and 800°C, but still strongly oxidizing to zinc vapor. As cadmium boils at 778°C, the vapor pressure would be high enough to vaporize the metal, especially if a stream of gas swept away the metallic cadmium already suspended.

Utilizing the apparatus sketched in Figure 2, the following run was made: 1500 grams of the calcine of Test 2 was used. This was held in the neighborhood of 750 to 800°C for 9 hours, with an average gas circulation (following Mr. Maier's suggestion of a low gas circulation) of about 100 cc. per minute for 7.5 hours, and then the rate was speeded up to 300 cc. per minute for 1.5 hours, to completely sweep out any vaporized cadmium present.

The calcine from this determination weighed 1267.5 grams. The explanation of this tremendous loss of weight--15% of the initial weight--is hard to account for. We have a loss of only 40 grams of sulphur, 17 grams of zinc, and 7 grams of cadmium, with 20 grams of lead; although the iron was reduced from the ferric to the ferrous oxide, judging from the color change from red to black. This cannot be a mistake in weighing, for barely 2% of the zinc is lost.

The fact remains--the cadmium disappeared; only 14.5% of it remained in the calcine, as can be seen in Table IV, Test 21; but none of it was collected in the baghouse, due probably to incorrect apparatus for the fume collection. This is the point where the next experiment is to be aimed--the collection of at least a portion of the cadmium inthe fume.

This test was projective, and has no further proof to back it up, due primarily to the necessity of completion of this thesis before the determination could be made. Future experiments will be conducted along this line to determine just why the cadmium was volatilized, and more important, where it disappeared after it was volatilized. I do not believe my analysis wrong; it was tried out in triplicate, and the checks were good. However, this is an exceedingly promising field for future exploration, to which the door has just been opened.

As to the commercial possibilities of the process, they are not just now apparent, as this was a purely scientific experiment, toward the collection of fundimental data. Moreover, future work may prove that somewhere in the determination, something was in error, and that the experiment was fruitless, tho an alluring mirage for a time.

E. Sulphide-Coke Reducing Tests.

During the preliminary runs, a test was made upon a mixture of 10% of coke and 90% of the sulphide ore, since cadmium behaves similerily to zinc, and zinc is reduced from the sulphide to some extent by coke:

$$2\,ZnS + C = 2\,Zn + CS_2.$$

A surprising thing was discovered in this preliminary determination--the fume collected in the bag assayed about 2% cadmium, considerably more than the average content of this fume, and for this reason, the following series of determinations were made:

Test 22: 6000 grams of "D" sample was thoroughly mixed with 1000 grams of coke, the resulting mixture heated to 1000°C, and the roast continued for 5 hours at this temperature. The results are tabulated in Tables III, IV, V, and VI; the composite results upon the zinc, lead and cadmium in Table XXIII. The calcine weighed 4761 grams; there was 197 grams of fume. It seems that the cadmium and lead are both taken out to a noticeable extent by this treatment, but at a considerable cost in zinc.

Table XXIII.

Removal ~~Resume~~ of cadmium & lead ~~Cd, Pb, and Zn in the Sulphide-Coke Reducing Tests.~~ from Unroasted Zinc Concentrate by Reducing Coke

Test	Time heating hours	Temp- heating °C	% Coke added grams	Percent total element caught in the fume			Percent total element in the calcine.		
				Pb	Cd	Zn	Pb	Cd	Zn
22	5 Hr.	1000°C	1000 g.	22.7	11.45	1.22	35.3	43.4	83.4
23	5.33	1100	1000	28.1	26.5	3.07	49.3	35.7	91.0
24	5.0	1200	1000	58.9	26.2	12.7	4.8	47.2	62.8
25	5.08	1100	500	37.7	24.2	2.05	27.5	67.3	90.3

Test 23: Advancing the temperatures to 1100°C, a duplicate roast of Test 22 was carried out. Here, we get 65% of the cadmium and 50% of the lead volatilized, with only 9% loss in zinc to the calcine. Comparison with Test 6 shows that considerable lead is retained in the calcine, due to the relatively non-volatility of the metallic lead formed during the reaction:

$$2\ PbO + C = 2\ Pb + CO_2.$$

but that the cadmium content has been reduced 15% below that of Test 6. Conclusions are therefore that the action of the coke retards the volatilization of lead, but accelerates the volatilization of the cadmium, and effects the overall recovery of zinc but little.

Test 24: While the general inefficiency of the 1200°C roasts had become firmly rooted in our minds, it was determined to make a trial at this temperature, viewing the favorable conditions at 1100°C. The conditions are the same as in Test 22, save that the temperature was maintained at 1200°C for 5 hours. From the viewpoint of the zinc, the results were disasterous. Almost 40% of the zinc was lost, as revealed by the calcine recoveries. Strangely, though, the lead was reduced to 5% of the original content, but the calcine retained 47% of the original cadmium. This determination is automatically rejected because of the excess zinc volatilized.

Test 25: Drawing the experimental work to a close, it was thought best to secure a comparison to the other runs by using a lower coke charge. As 1100°C shows up so favorably before, this temperature was chosen. 6000 grams of the sulphide ore was treated with 500 grams of coke (the amount utilized in the oxide- coke reduction tests) and held at 1100°C for 5.08 hours. The lead in the calcine drops; the cadmium takes a decided raise. To get the general idea of the relationship between the whole series of determinations, we take the 1100°C determinations from each (Tests 6, 11, 23, and 25) and place them in Table XXIV.

Table XXIV.

Volatilization of Lead, Cadmium and Zinc from Zinc concentrate

~~Relationship of the Oxide, Reducing, and Sulphide~~

~~Reducing Tests~~ at about 1100°C, as oxide, and on adding Coke to Oxides and Sulphides

Conditions of Volatilization: Test	Grams Coke added	Fume, percentage of Total Element present			Calcine, percentage of Total Element present.			Time Roast hours oxide
		Pb	Cd	Zn	Pb	Cd	Zn	
as ~~6~~ oxide →		36.5	20.25	1.12	36.4	51.1	94.8	4
coke added ~~11~~ to oxide →	500	19.25	25.8	6.38	56.0	51.7	82.4	4
coke added ~~23~~ sulphide	1000	28.1	26.5	3.07	49.3	35.7	91.0	–
" " ~~25~~ "	500	37.7	24.2	2.05	37.5	63.7	90.3	–

Reviewing the table above, it is seen that the reducing roasts have a tendency to eliminate possibly a slight bit more cadmium, that the zinc recovery is below that of the oxidizing roasts as shown in Table XVI, and that the lead volatilization is definitely checked by the presence of coke. We must, because of the facts as presented above, conclude that, in general, coke when added to either the raw sulphide ore or to the oxidized sample has some little effect on the cadmium, and has a retarding effect upon the lead.

It has been evident throughout this series of attempted reducing tests: (1) That some cadmium has been reduced by the coke, and volatilized at (2) the expense of considerable retention of the lead in the calcine. The coke, at the best, is therefore an uncertain factor, adds but little to the properties of the volatilization of the cadmium, barely 5% more cadmium being volatilized, and has a negative effect on the lead, holding in the neighborhood of 15% more of this element in the calcine (Table XXIV). We are therefore holding the two elements on the pans of a balance--when one goes down, the other goes up, with the use of coke.

As between the sulphide and oxide reducing roasts, Table XXIV shows more volatilization of the lead during the sulphide roast, but that, amounts of coke equal, less cadmium remains in the calcine of the oxide reducing roasts. The zinc balance is very much in favor of the sulphide roast, as a very large percentage of the zinc is accounted for at the end of the determination.

The sulphide ore as a reducing agent did not develop the hoped-for reaction, and might be rightly classified as a modified oxidation roast, although considerably more zinc was volatilized than in the oxide roasts, and the cadmium results a toss-up, while the lead was negatively effected.

F. Study of the Forms in which the Cadmium Occurs in Fume and Calcine.

We have demonstrated that cadmium can be volatilized from zinc concentrates in a variety of ways, but at the best, considerable remains in the calcine. The question naturally arises (1) In what form is the cadmium volatilized, and (2) In what form does it remain in the calcine? While this question is not directly in line with the problem, some work has been done upon these two questions, towit:

(1) The form in which the cadmium occurs in the fume, and is volatilized. From the theoretical considerations, we have seen that only two volatile constituents of cadmium are present--cadmium sulphide and cadmium oxide. Which of these is present, in the fume, and to what extent?

As can be seen from page 30, cadmium sulphide is insoluble in a 5% solution of HCl, while cadmium oxide is soluble in the acid at any concentration.(1) Hence, the following treatment was evolved: To 10 grams of the fume, add 100 cc. of 5% HCl solution, hot, and let react. Filter off the residue, and treat with another 100 cc. of hot 5% HCl; repeat until no more zinc can be detected in the filtrate with potassium ferrocyanide. Analyze the residue for Cd, and figure as CdS. Table XXV gives the results obtained upon one oxidizing and two reducing roasts, taken as average samples of the fume.

Table XXV very conclusively proves that the fume contains the cadmium in the oxide form to 99.9%, and since the similarity of the

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(1) Mellor, Loc.Cit. v.4 p 515.

Table XXV.

Percentages of Cadmium as the Oxide and Sulphide in the Fume.

Test	Grams Heads	% Cd Heads	Grams Cd Heads	Grams Cd Residue	% Cd as CdS	% Cd as CdO
7 (1)	10	1.50	.150	.0015	.10	99.90
(2)	10	1.50	.150	.0024	.16	99.84
(3)	10	1.50	.150	.0017	.11	99.89
13 (1)	10	3.98	.398	.0019	.05	99.95
(2)	10	3.98	.398	.0020	.05	99.95
(3)	10	3.98	.398	.0020	.05	99.95
22 (1)	10	2.24	.224	.0020	.09	99.91
(2)	10	2.24	.224	.0021	.09	99.91
(3)	10	2.24	.224	.0021	.09	99.91

curves of the vapor pressure of cadmium oxide, and the rate of volatilization from the calcine are so nearly identical, it is therefore almost conclusively proven that the cadmium ix volatilized under all conditions as the oxide.

The above table does not take into consideration the formation of sulphates or sulphites in the fume after it has been deposited, altho Budgen gives 40% of the fume as soluble sulphate.(1) Apparently, too, cadmium is volatilized from the lead blast furnace as the sulphide, due to the color of the fume.(2) It has already been demonstrated (page 15) that the volatilization as the sulphate is probably impossible, due to the decomposition of the sulphate.

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(1) Budgen, Loc. Cit. p 13.

(2) Ibid, p 31.

(2) Turning to the composition of the cadmium in the calcine, the question of cadmium ferrites comes up. We find them reported by Hanley and others.(1)

In attempting to find a method whereby the possibility of cadmium ferrite could be determined, it was found that cadmium sulphate is very soluble in both water and sulphuric acid;(2) that cadmium sulphide is soluble in ammonium chloride solutions,(3) and cadmium oxide is soluble in ammonia, water, and ammonium chloride.(4) Assuming the residue present as cadmium ferrite, which would be involatile, the other forms being volatile under normal circumstances, I leached 10 grams of the calcine in 200 cc. of Low's solution for two hours at 35°C, with constant agitation, and analyzed the residue for cadmium, and assumed it present as cadmium ferrite. The results in Table XXVI were obtained:

Somewhat fine Same

Table XXVI.

Cadmium in Calcine as Cadmium Ferrite, by Analysis Above:

Test.		Gm. Hds.	% Cd Hds.	Gm. Cd. Hds.	Gm. Cd Tails	% Cd as Ferrite.
7	(1)	10	.10	.010	.0014	14.0%
	(2)	10	.10	.010	.0020	20.
	(3)	10	.10	.010	.0015	15.
14	(1)	10	.16	.016	.0043	27.
	(2)	10	.16	.016	.0028	17.5
	(3)	10	.16	.016	.0034	21.

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(1) Hanley, Clayton & Walsh, Formation of Insol. Zn compounds during roasting. Tech. Pub. # 220, A.I.M.M.E.

(2) Mellor, v.4 p 627-28.

(3) Ibid, v.4 p 605.

(4) Ibid, v.4 p 553, 518.

From the figures given in Table XXVI, it would seem that approximately 20% of the cadmium left in the calcine is insoluble in Low's solution---or is probably present as the ferrite.

G. The Separation of Lead and Cadmium in the Fume.

While considerable work was done in an effort to accomplish the separation of lead and cadmium by volatilization, little was accomplished toward this end.

(1) The differential seperation between 700 and 1000°C was a failure (page 49).

(2) A lead was given in Test 13, when it was found that the pipe dust alone analyzed 3.98% cadmium, and 6.6% lead, in the reducing fume, while that of Test 14 held only .87% cadmium in the total baghouse fume, to 4.4% lead. This was disproved by Test 20, when the 432 grams of baghouse fume held an average of 1.26% cadmium, while the pipe dust weighed 212 grams, and assayed .84% cadmium. It is therefore definite that this method of separation (or rather, partial separation) is futile.

(3) A slight effect might be secured by the use of coke to keep the metallic lead in the calcine, and allow the metallic cadmium to volatilize off, but as seen on pp 75-76, this would not approach even a resemblence of a commercial process.

It is therefore seen that no method of separation of the lead and cadmium during the volatilization process has been developed.

Conclusions.

1. That the optimum temperature for the elimination of sulphur from zinc concentrates is about 950°C.

2. That lead can be volatilized from zinc concentrates, and that the rate of volatilization closely follows the vapor pressure curve of lead oxide.

3. That the volatilization of lead from either oxidized or sulphide concentrates is reduced by the addition of reducing agents.

4. That a quantative method of determining cadmium has been developed that is accurate to from .02% to .05% of the cadmium content of any zinc concentrate, fume, or calcine.

5. That cadmium can be volatilized from zinc concentrates, and that the rate of volatilization closely follows the vapor pressure curve of cadmium oxide.

6. That cadmium is volatilized almost completely as the oxide.

7. That the presence of reducing reagents increases the volatilization of cadmium from the calcines, but that this is not marked enough when solid materials are used as reducers, but that the reaction is largely masked by the overwhelming preponderence of zinc.

8. That the higher the temperatures of oxidizing roasts, the greater the volatilization of both the lead and cadmium, both approaching complete volatilization between 1320 and 1350°C within four hours after this temperature is reached.

9. That for commercial purposes, oxidizing roasts at about 1100°C is the most feasible method of removing the greater portions of sulphur, lead, and cadmium from the calcine, but that the formation of zinc ferrites is greater at this temperature, and that more zinc than the theoretical ratio is held insoluble by the iron in the high-temperature roasts.

10. That there are great possibilities in the vaporization of cadmium as the element from previously calcined material, when treated between 750 and 800°C for a long period of time with a mixture of 95% carbon monoxide and 5% carbon dioxide, with a low gas circulation, but that hasty conclusions should not be reached upon this point, and that future investigations should be made upon it.

11. That zinc oxide is inappreciably volatile below 1320°C.

12. That no feasible method for separation of lead and cadmium has been developed in the problem.

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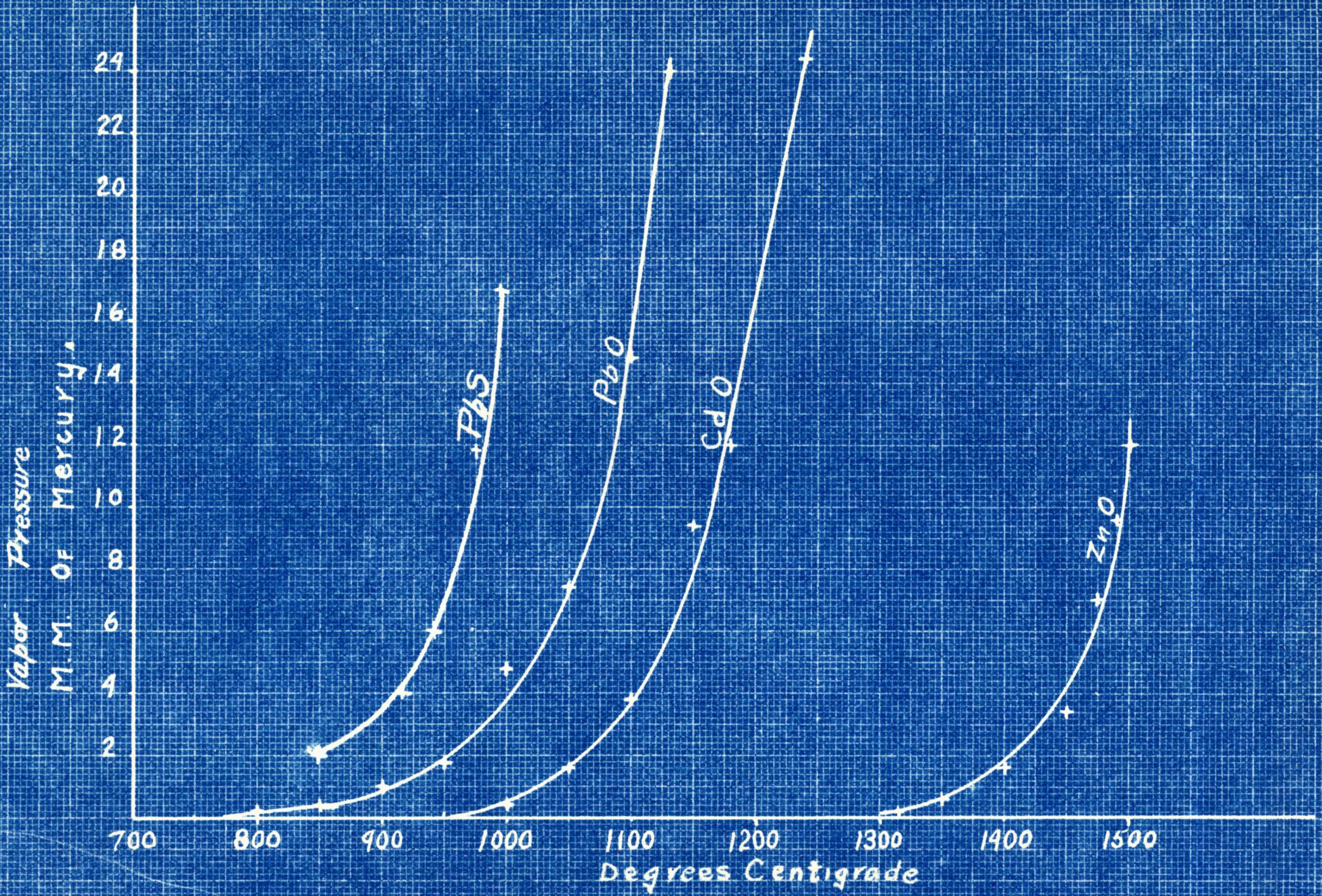
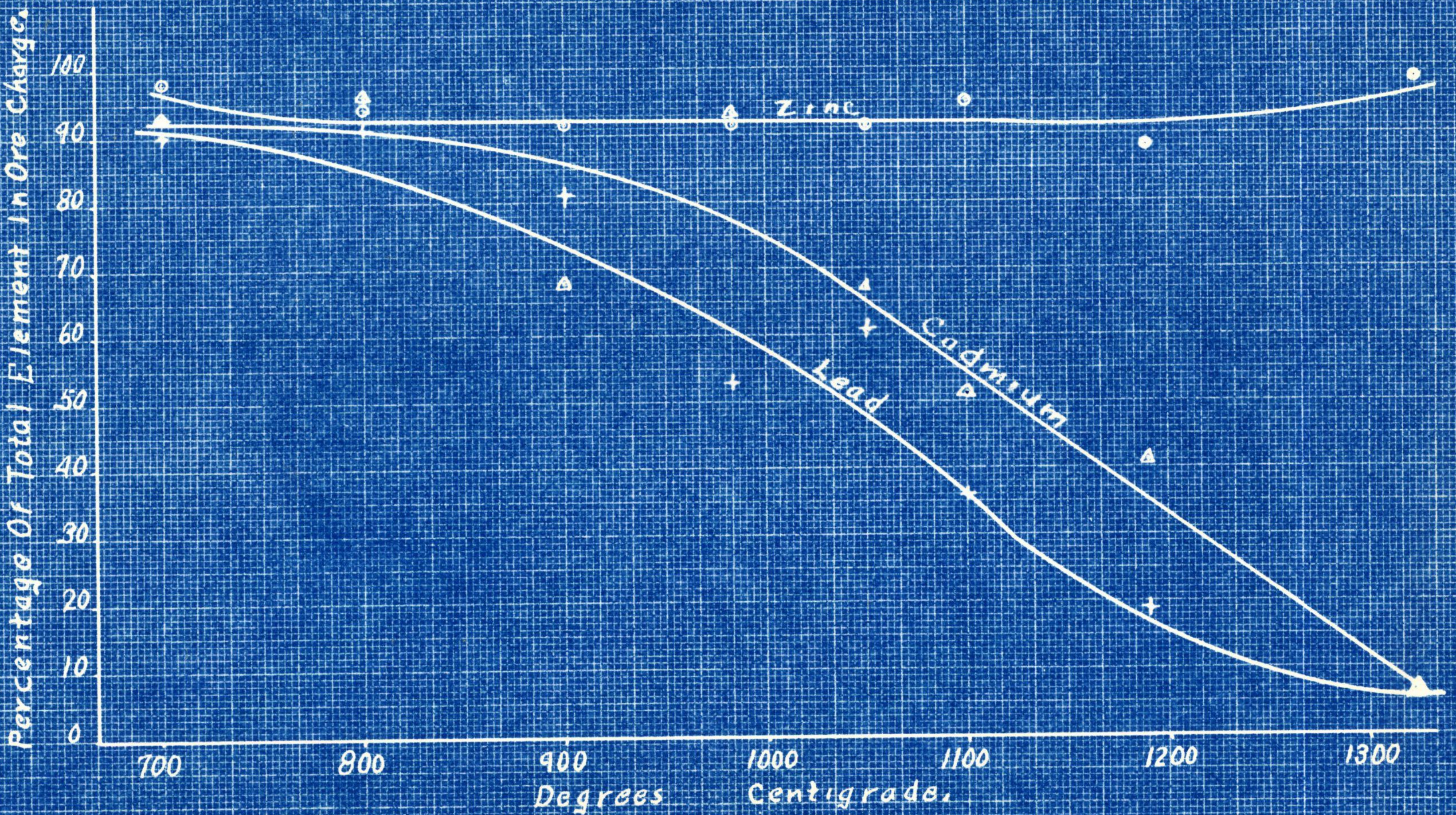


GRAPH I. VAPOR PRESSURES OF ZNO, CDO AND PBO. (Feiser)

PBS (Schenck and Albers)



Graph II Pb. Cd. and Zn In Calcine

SEP ATION of LEAD and CADMIUM by VOLATILIZATION s OXIDE