THE PRECIPITATION OF ZINC FROM SULFATE SOLUTIONS

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OF
ZINC FROM SULPHATE SOLUTIONS

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INTRODUCTION

The work of this thesis was carried on in the Metallurgical Research laboratories of the University of Utah, in connection with the U. S. Bureau of Mines. The work was under the direct supervision of O. C. Ralstonn, who is Metallurgist at the Salt Lake Station. Valuable assistance was received from Dr. R. H. Bradford of the University, D. A. Lyon, former Chief-Metallurgist, A. E. Wells, present Chief-Metallurgist, and J. C. Morgon, Junior Chemist, of the Bureau of Mines, The work on the precipitation of solutions made from the leaching of roasted ores was carried on with C. W. Frith, a Fellow in the Department of Metallurgical Research.

LEACHING OF ZINC ORES

The leaching of zinc ores has in recent years had an important place in the metallurgy of that metal. Many zinc ores have been found unsuited for mechanical concentration. The chief difficulty in their mechanical concentration has been to secure a good grade of concentrates that would be free from large quantities of iron or lead. Smelters of zinc penalize for iron and will not pay for the lead content.

Leaching of these ores, mainly with sulphuric acid has solved the difficulty of extracting the zinc from these ores. After leaching however, the problem of recovering the zinc from the solutions has to be solved. In many cases electrolytic deposition similar to that employed in the recovery of copper has proved successful. Difficulties have been encountered in the development of the electrolytic process which have made that process unsuited for use in the recovery of zinc from ores in certain localities.

The conditions for successful electrolytic work are cheap power and good extractions. Many plants would not be able to operate if they did not have lead and silver in the ore which they extract in addition to the zinc. These conditions will not be found entirely filled at any mine or mill. Still a large number will be able to operate successfully and be a competitor to the zinc smelter. The power consumption will always be high for each pound of zinc extracted in comparison the consumption for other netals that are extracted electrolytically. The owners of large low grade properties must wait for a cheaper process; one in which they will not need the presence of other metals to make the treatment of the ore profitable.

The work of this thesis was carried on with the idea of finding some method of chemical precipitation of zinc from its solutions, in which the cost per pound of zinc would be low enough to warrant the working of many ores which are at the present time practically worthless. Utah has a large number of ores of this type and if such a process could be worked out, the resources of this State would be increased to a large extent.

ANALYTICAL METHODS

All solutions were analysed for zinc and iron, both before and after precipitation. The solutions from ores that contain manganese were analyzed for that metal. The precipitates were analyzed for zinc, iron, manganese, chlorine, lime, and magnesia. I have incorporated the methods of analysis in this thesis.

Zinc and Iron in Solution.

Zinc and iron are determined from the same sample if there is little or no manganese in the solution. A separate sample ought to be taken for iron if there is much manganese in the solution.

A sample is taken from the solution, the valume of which is dependent on the amount of zinc in solution. The sample should be of such volume that not much more than 100 cc of ferrocyande will be required to titrate the zinc. The amount of sample canbe approximated from a knowledge of the solutions used.

Add bromine water to the solution, make ammonical and boil but do not drive off all of the bromine. Filter and wash well with hot water. Make filtrate acid with hydrochloric acid, using 5 cc. excess. Heat to boiling, add hydrogen sulphide water to precipitate the copper and the other base metals. Titrate the solution hot with potassium ferrocyanide.

Dissolve the iron precipitate, if little or no manganese is present, in hydrochloric acid. Do not have over 5 cc. excess. Reduce hot with stannous chlorideand dilute to about 700 cc. with cold water. Add mercuric chloride to oxidize the excess stannous chloride. Titrate with potassium permanganate.

If manganese is present in large amounts, determine iron separately by boiling out all the bromine water, add ammonia, filter out the ferric hydrate and proceed for iron as outlined above.

Zinc and Iron
(Zinc Precipitate)
(Calcium Sulphate Precipitate)

Dissolve half gram sample in hydrochloric acid. Proceed as in the analysis of zinc and iron in solutions.

Lime and Magnesia
(Zinc Precipitate)

Dissolve half gram sample in 10 cc. hydrochloric acid. Take to dryness. Take up with hydrochloric acid and water, add ammonium chloride and make ammonical. Filter and wash. Bring to boiling, add ammonium exalate and boil for 10 minutes. Filter and set aside the filtrate. Dissolve the precipitate in hydrochloric acid, make ammonical and add a small amount of ammonium oxalate. Filter and wash. Combine the filtrates, add 5 - 7 cc. of sulphuric acid to 400 cc. of water and bring to a boil. To this add filter paper containing the precipitate and titrate the lime with permanganate. The lime value is half the iron value of the pefmanganate.

Take the filtrates down to dryness in a casserole. Take up with hydrichloric acid, add ammonium chloride and ammonia. Boil, add sodium ammonium phosphate. Allow to set for four hours. Filter and wash the precipitate. Burn off in a muffle.

The weight of the precipitate multiplied by 0.3624 gives the weight of magnesia.

Manganese

(Zinc Precipitate)

Dissolve half gram sample in 10 cc. sulphuric acid. Take to dryness. Take up with water and boil. Make slightly alkaline with sodium carbonate. Make neutral with the addition of zinc oxide in excess. Dilute to about 700 cc. and titrate hot with permanganate.

The iron value multiplied by 0.2924 gives the manganese value of the permanganate.

Manganese
(Solutions)

Add sulphuric acid to 25 cc. sample. If calcium sulphate separates out, boil for a time and filter. Add more sulphuric acid and take to dryness. Proceed to dilute and neutralize as in the analysis of a precipitate. Titrate as before with permanganate.

Chlorine
(Zinc Precipitate)

Take a sample of from two to five grams. Add 50 cc. warm water and two to five cubic centimeters of nitric acid. Warm but do not boil. Neutralize with precipitated calcium carbonate. The solution may be lightly alkaline. Two methods may be used for completing the determination.

1. Add two cc. of two per cent potassium chromate solution. Titrate with silver nitrate to a faint pink tinge. This method is not advised as the endpoint is difficult to see.

2. Use two per cent potassium chromate solution as an outside indicator.

Dissolve 16.966 gm. silver nitrate in one liter of solution to make the titrating solution.

Preliminary Tests in Zinc Precipitation.

Object:

Before making a series of precipitation tests a number of trial tests were made to see if it would be advisable to use certain precipitants.

Method:

Zinc solutions were made of zinc chloride and zinc sulphate. In all cases the amount of precipitant used was more than sufficient to care for all the radicals to be precipitated. The required amount of precipitant theoretically calculated is known as one equivalent and will be so written throughout this thesis.

Conclusions:

1. An excess of lime will precipitate all of the zinc from a solution of zinc chloride.

2. An excess of lime will precipitate all of the zinc from a solution of zinc chloride which has been made from a solution of zinc sulphate.

3. It is possible to change a zinc sulphate solution to a zinc chloride solution by the addition of calcium chloride and the precipitation of calcium sulphate.

4. An excess of lime will precipitate over 90 per cent of the zinc from a mixed solution of sulphate and chloride.

5. Magnesium carbonate in excess will precipitate nearly all of the zinc from a zinc chloride solution.

6. An excess of sodium sulphite nearly all of the zinc as zinc monosulphite from a zinc chloride solution.

Calcining of Zinc Precipitates.

Object:

It was desireable to know how high the zinc content of a precipitate could be made by calcining it to the oxide or a mixture of the oxide and sulphate. We also wished to know whether any zinc would volatilize. The calcining of a precipitate would be necessary if the zinc was to be reduced in retorts.

Method:

Both precipitates of zinc sulphite and zinc hydrate were used. Calcination was carried on in a gas muffle at a temperature of 800° - 900° C. Twenty grams were used in most cases. The time of calcining was two hours.

Conclusions:

1. Calcining of zinc sulphite is possible without the loss of zinc.

2. The zinc sulphite calcine is a mixture of oxide and sulphate.

3. Zinc is lost in the calcination of zinc hydrate. This is probably due to the volatlization of zinc chloride which is present in the precipitate. Analysis showed the presence of chloride. It is present as a basic chloride of zinc.

Calcination Table

Table 1.

#	Wt Ppt.	Wt. Calcine	Zn %	Loss Gm	Loss %	Ppt.
1	20	12.5960	51.8	0.00	0.00	Zinc Sulphite
2	20	12.0154	51.8	0.29	4.60	" "
3	20	12.9400	68.3	1.48	14.3	" Hydrate
4	20	11.5300	59.2	1.85	21.3	"

Precipitation of Zinc

from Zinc Chloride Solutions with Lime

Object:

Lime is an inexpensive material and easily slacks to the hydrate. It offers itself as a suitable precipitant of zinc from solutions which do not contain radicals which will precipitate with the calcium of the lime. These tests were carried out to see what grade of precipitate could be obtained, The amount of zinc that would be removed from solution, and the amount of lime that would be retained by the presipitate.

Method:

Before carrying out these tests it was necessary to prepare a solution of zinc chloride. This was done by dissolving mossy zinc in hydrochloric acid. The solution was diluted to make approximately five and ten per cent solutions. Lime in the equivalents shown in Table 1 was then added and the solutions agitated for 24 hours. The precipitate was filtered, dried weighed, and analyzed for zinc, lime, and magnesia.

Conclusions:

1. Lime precipitates zinc in approximate porportion to the equivalents used.

2. When the equivalents used are increased the grade of precipitate decreases. The lime and magnesia content increases and the zinc content decreases.

3. The extraction in a weak solution is greater than in a strong solution of zinc and the grade of precipitate is better.

4. The precipitates from a ten per cent solution were difficult to handle due to being sticky. The five per cent solution gave no such trouble.

5. It is possible to precipitate all the zinc from a chloride solution if an excess of lime is used.

6. The main idea of future tests should be to work for a precipitate with lower lime and magnesia content.

7. The magnesia content in the lime used lowered its precipitating efficiency.

8. Fine grinding of the lime or preparation of a milk of lime from well calcined limestone, facilitates the precipitation.

Table 2

(Following Page)

Table 2.

Lime Precipitation of Zinc.

No.	Sol gm Zn	Vol	Lime added	eq.	wt. Ppt	% Zn	Ppt Gm Zn	Bm Zn Sol
1	24.35	500	11.30	0.5	21.50	57.7	12.40	-- --
2	"	"	13.50	0.6	27.90	53.8	15.00	-- --
3	"	"	15.80	0.7	33.40	53.6	17.90	6.22
4	"	"	18.00	0.8	37.70	53.7	20.20	3.14
5	"	"	20.30	0.9	44.00	51.5	22.60	1.88
6	20.90	430	19.50	1.0	40.60	51.6	20.96	0.09
7	46.95	500	22.60	0.5	54.80	49.8	27.30	20.20
8	"	"	27.10	0.6	58.60	49.8	29.20	15.70
9	"	"	31.60	0.7	68.20	52.8	36.00	11.70
10	"	"	36.10	0.8	82.90	46.0	38.10	6.67
11	"	"	40.70	0.9	103.00	41.6	42.80	2.95
12	"	"	45.20	1.0	103.00	43.4	44.70	0.55

Table 2 (cont)

Lime Predipitation of Zinc

No.	Total Zn	Ext. Ppt.	Ext. sol.	Ppt. % CaO	Ppt. % MgO
1	-- --	51.0	-- -	1.50	2.03
2	-- --	61.8	-- -	1.98	2.39
3	24.12	73.7	71.6	1.95	2.22
4	23.34	83.2	87.2	2.18	2.06
5	24.48	93.0	92.3	2.76	3.51
6	21.05	100.3	99.5	3.06	4.30
7	47.50	58.0	57.0	2.62	2.26
8	44.90	62.2	66.8	3.18	3.84
9	47.70	76.7	75.1	2.38	2.51
10	44.77	81.2	85.8	4.47	4.03
11	45.75	91.2	93.7	5.42	4.42
12	45.25	95.5	98.8	5.31	4.82

Lime analysis

CaO. . . .47.4
MgO. . . 29.9

Precipitation of Zinc from Chloride Solutions withMagnesia.

Object:

These tests were carried out to see if magnesia was as efficient for the precipitation of zinc as lime.

Method:

The same method of running the tests was used as with the lime precipitation.

Conclusions:

1. The magnesia precipitated all of the zinc.

2. The magnesia precipitate catains a higher percentage of zinc than the lime precipitate.

3. The magnesia content of the precipitate was higher than expected. The per cent of magnesia must be lowered a large amount before magnesia precipitation can be used.

4. The precipitant used was not completely calcined. This may account for the high magnesia content of the precipitate.

(Table 3)

Table 3.

Magnesia Precipitation of Zinc.

No.	gm Zn sol	vol	eq.	MgCO gms	Wt. Ppt	% Zn	Ppt. gm Zn.	Sol gm Zn	Total Zn	Ext. Ppt	Ext. Sol.	Ppt. % MgO	Ppt. % CaO
1	48.76	500	0.5	20.00	54.2	52.8	28.60	19.50	48.20	58.7	59.8	19.08	nil
2	"	"	0.75	30.20	75.20	54.7	41.20	7.65	48.85	84.5	84.3	6.00	"
3	"	"	0.90	36.20	89.10	53.8	48.00	0.52	48.52	98.5	98.9	20.90	"
4	"	"	1.00	40.20	101.30	49.7	50.50	0.34	50.84	104.0	99.3	25.24	"
5	"	"	1.10	44.20	140.6	39.2	54.80	0.34	55.14	112.0	99.3	28.20	"
6	25.44	"	0.50	10.50	24.8	58.4	14.50	12.05	26.55	56.8	52.8	24.30	"
7	"	"	0.75	15.75	44.6	53.4	23.80	4.61	28.41	93.4	81.9	19.90	"
8	"	"	0.90	18.90	44.3	56.0	24.8	0.73	25.53	97.0	97.2	31.40	"
9	"	"	1.00	21.00	49.2	53.7	26.4	0.16	26.56	103.5	99.4	29.20	"
10	"	"	1.10	23.10	65.8	48.5	31.90	0.27	32.17	125.0	98.9	36.00	"

Tests 5, 7, and 10 did not check on total zinc. This was probably due to a mistake in recording of weights.

Removal of Sulphate. from Zinc Solutions with calcium Chloride.

Object:

These tests were made to determine the amount of sulphate it is possible to remove from a zinc sulphate solution by precipitating as calcium sulphate. It is necessary in lime precipitation to work with a chloride solution and accordingly we must change the solutions made by sulphuric leaching to a solution of zinc chloride.

Method:

Bullion Coalition #13 was leached to obtain a zinc sulphate solution. The total sulphate in the solution was determined and the required amount of calcium chloride calculated. Equivalents of .5, .6, .7, .8, .9, 1.0, 1.1, were used. One precipitation was made in which the calcium chloride was first put in solution before it was added to the sulphate solution.

Conclusions:

1. Five-tenths of an equivalent will precipitate one half of the sulphate in the solution. As the number of equivalents is increased the amount of sulphate removed increases but not in the same porportion.

2. One equivalent removes 87.2 per cent of the sulphate. One and one-tenth will remove 93 per cent of the sulphate.

Removal of Sulphate.

(cont)

3. The amount of zinc retained by the precipitate decreases with the amount of sulphate precipitated. No zinc was retained by the precipitate when one equivalent was used.

4. The process can be made cyclic since there will be a regeneration of calcium chloride when the zinc is precipitated with lime.

(Table 4)

Table 4.

Removal of Sulphate.

No.	Vol	sol Gm Zn	Gm SO_4	eq. $CaCl_2$	wt. Ppt	% Zn	Gm Zn.	lost % Zn	sol Gm SO_4	% SO_4 Pptd.
1	400	16.95	46.90	0.5	35.1	0.56	0.20	1.18	23.4	50.2
2	"	"	"	0.6	39.8	0.51	0.20	1.18	19.3	58.8
3	"	"	"	0.7	44.8	0.15	0.07	0.41	16.1	65.7
4	"	"	"	0.8	52.1	0.05	0.03	0.18	11.9	74.6
5	"	"	"	0.9	65.1	0.05	0.03	0.18	8.6	81.7
6	"	"	"	1.0	71.1	nil	nil	nil	6.0	87.2
7	"	"	"	1.1	70.4	nil	nil	nil	3.3	93.0

Preliminary Precipitation Tests

(Impure Solution)

Objedt:

These tests were run to try the precipitation of zinc from solutions that contained various impurities.

Method:

The general scheme of making these tests was to first clear the solution of all sulphate possible with calcium chloride, next to precipitate all of the iron with limestone, and recover the zinc by the use of slacked lime as a precipitant.

Results:

The tests run as outlined above gave a dark precipitate when agitated over 4 hours. Analysis of these precipitates showed the presence of manganese, in one case as much as 4.42 per cent being found. Ferrous sulphate and bleaching powder were used separately to try and eliminate the manganese. The amount of manganese was lowered. No precipitate was made however that was not colored.

Conclusions:

The problem for the most work will be the elimination of manganese from the precipitate and the production of a precipitate which is not colored. It can be supposed that the soloration is due to the manganese to a large extent. Some is likely caused by the presence of iron. The limestone was able to remove practically all of the iron from the solution. The precipitate contained more than the allowable amount of lime and magnesia. This presence of lime and magnesia is always high if all of the zinc is to be precipitated.

Lime Paste Precipitation

(Solution Made from Western Mining Ore)

Object:

It was desirable to know what effect length of time would have upon the precipitation of zinc from impure solutions, and whether increasing the length of time would increase the impurities in the final precipitate.

Method:

Two separate tests were run on this solution. In the first test the lime used was slacked in beakers separately for each precipitation, the equivalent amount of lime being used in each case. In the second set the lime was first slacked and then made into a paste which was used. The sulphate and the iron was removed as in the previous tests.

Conclusions:

1. Less than two-thirds of the zinc will be precipitated if the solution is agitated for one hour or less.

2. An extraction of 80% is obtained by agitating for two hours. The lime content is too high.

3. If the solution is agitated for four hours or more, the precipitate becomes very dark and manganese

is thrown out. Iron cannot have much effect on the coloration of the precipitate since the white precipitates contained nearly as much iron as those that were colored.

4. Unslacked lime added to solutions does not precipitate zinc as readily as when it is added as a paste.

5. The lime paste used should be of such strength that one cc. is equivalent to about two-tenths of a gram of zinc.

6. The chlorine content is variable. When complete precipitation is obtained, six to seven per cent of chlorine is present. It is partially present as the basic chloride of zinc.

7. The zinc contained in the precipitates of the iron and the sulphate is negligable.

8. Some method must be worked out whereby the lime content can be reduced to two per cent or less.

(Table 5.)

Precipitation with Lime Paste

(Western Mining)

Table 5.

No.	Time	CaSO4 Gm Zn	Fe Ppt gm Zn	Wt Zn Ppt	% Zn	% Mn	% Fe	% CaO
1	5 min	0.33	0.13	21.8	23.3	0.049	0.23	37.4
2	10 "	0.07	0.18	18.0	26.4	Tr	0.47	35.0
3	20 "	0.35	0.18	19.5	25.0	0.098	0.23	35.2
4	40 "	0.24	0.09	22.2	30.8	nil	0.33	28.4
5	1 hr.	0.30	0.11	22.0	34.1	nil	0.48	26.9
6	2 "	0.31	0.09	22.5	40.0	Tr	0.47	22.4
7	4 "	0.27	0.12	23.5	41.0	2.18	0.70	13.5
8	8 "	0.26	0.13	20.3	51.7	2.16	0.42	6.57

% MgO	% Cl	Ppt gm Zn	Sol Gm Zn	Total gm Zn	Ext	$
1.47	6.75	5.01	4.69	10.16	44.6	1
2.40	3.90	4.75	5.20	10.21	42.3	2
1.45	4.08	4.88	4.62	10.03	43.4	3
1.04	5.96	6.85	3.89	11.07	60.9	4
1.25	8.66	7.50	3.42	11.33	66.7	5
0.47	7.81	9.02	2.00	11.42	80.2	6
5.68?	6.66	9.63	0.13	10.15	85.5	7
3.53?	6.04	10.50	0.13	11.02	93.4	8

11.25 grams of zinc in original solution

Oxidation of Manganese with Bleaching Powder.

Object:

It was thought that manganese could be eliminated from the solution if the solution was oxidized by some means. It was though that the chlorine liberated from bleaching powder would be one of the best oxidizing agents for this purpose.

Mrthod:

Calcium chloride was added to precipitate the sulphate. Bleaching powder was then added, the mixture agitated for a time and the precipitate filtered out. Limestone was then added to precipitate the iron. Sulphuric acid was then added in various equivalents to the bleaching powder to liberate the chlorine.

Conclsusions:

1. A white precipitate can be obtained when bleaching powder is added to the solution.

2. The precipitate isnearly free from manganese and iron.

3. The lime content was high in porportion to the amount of zinc precipitated.

4. The chorine was about the same as in the previous tests.

(Table 6)

Oxidation of Manganese
(Bleaching Powder)

Table 6.

No	eq. acid	CaSO4 gm Zn	Fe Ppt gm Zn	% Total	Wt. Zn Ppt	% Zn	% Mn	% Fe
1	- ---	Tr	0.71	4.65	32.5	38.1	.07	.09
2	0.125	"	0.55	3.61	30.1	37.1	.04	.22
3	0.25	"	0.43	2.82	32.2	36.5	.04	.17
4	0.50	"	0.32	2.10	32.5	36.5	.035	.31
5	1.00	"	0.31	2.03	37.8	32.6	.035	.13
6	1.50	"	0.33	2.16	34.1	39.2	.021	.13
7	2.00	"	0.21	1.38	33.9	37.8	.028	.17

No.	% CaO	% Cl	sol gm Zn	Total gm Zn	Ext.
1	21.55	11.82	2.82	15.91	81.2
2	20.90	9.24	3.48	15.21	73.3
3	19.75	9.56	3.12	15.30	77.0
4	20.85	8.51	3.34	15.51	77.8
5	20.60	9.66	2.52	15.13	80.7
6	19.90	11.78	3.05	16.73	87.5
7	19.05	10.25	3.22	16.23	83.9

Solution originally contained 15.25 gm of zinc per liter.

20# of bleaching powder used per ton of solution.

Use of Excess Bleaching Powder
to Remove Manganese

Object:

The solutions after treatment with 20# of bleaching powder per ton still showed the presence of manganese in the solution. These tests were made to see if the manganese culd not be removed entirely and a manganese product obtained.

Method:

The same method was used as with the other bleaching powder test.

Conclusions:

1. The addition of excess bleaching powder does not increase the removal of the manganese.

2. The resulting zinc precipitate was dark due to more manganese being thrown out.

3. The amount of chlorine was not as large as was expected considering the amount of chlorine liberated from the bleaching powder.

4. The lime and magnesia was not as high as when less bleaching powder was used.

Table 7.

Table 7.

Precipitation; Excess Bleaching Powder.

No.	Vol	Gm Zn	#/Ton	Wt. CaSO4	% Zn	Gm Zn	% Fe	% Mn
1	500	15.25	40	79.3	3.15	2.50	2.72	0.75
2	"	"	60	101.2	1.05	1.05	6.85	0.75
3	"	"	80	93.0	2.63	2.44	3.56	0.76

No	Wt. Ppt	% Zn	% Fe	% Mn	% CaO	% MgO	% Cl	Gm Zn
1	27.5	45.7	0.91	2.47	13.10	3.85	4.58	12.60
2	26.2	49.7	1.72	0.40	9.55	4.47	2.91	13.00
3	27.9	47.2	0.18	2.21	15.05	3.96	3.54	13.18

No	Sol. Gm Zn	Total Zn	Ext.
1	0.05	15.10	82.6
2	0.08	14.05	85.0
3	0.12	15.62	86.5

Removal of Lime and Magnesia with Zinc Chloride.

Object:

The precipitates obtained in the lime preciptation of zinc solutions contained too much lime to be sold on the market. This test was made with the idea that the contained lime would react with the zinc chloride and form more zinc hydrate with the formation at the same time of calcium chloride.

Method:

The precipitates obtained from the excess bleaching powder tests were agitated with the zinc chloride solution for four hours and the precipitate filtered.

Conclusions:

1. Zinc chloride will remove the larger part of the lime. If the preciptate treated does not contain over 15 per cent lime. In those cases the lime was reduced to less than two per cent.

2. The per cent zinc in the precipitate was raised and the weight of the precipitate increased. For some reason the manganese content dropped to a much lower per cent.

3. The residue in these tests was very hard and acted like cement.

Table 8.

Removal of lime and Magnesia.

Table 8.

No.	Wt Ppt	% Zn	Gm Zn	% CaO	% MgO	% Cl	% Mn	Wt. Res.
1	18.0	45.7	8.25	13.10	3.86	4.58	2.47	21.7
2	19.1	49.7	9.50	9.55	4.47	2.91	0.40	26.5
3	17.0	47.2	8.00	15.05	3.96	3.51	2.21	20.8
4	100.0	34.9	34.90	19.52	- --	- --	- --	120.7

No.	% Zn	Gm Zn	% CaO	% MgO	% Mn	% Cl
1	54.2	11.75	1.29	2.72	0.13	8.18
2	53.1	14.00	1.10	2.42	0.39	9.00
3	34.7	11.40	1.90	2.50	0.73	6.05
4	49.4	59.50	3.40	0.40	0.08	8.25

#4 was a mixture of several percipitates.

Removal of Manganese

by the use of Chlorine

Object:

In all the precipitations so far carried out with solutions containing manganese, the precipitate turned dark if agitated for a length of time sufficient to insure nearly complete precipitation. This test was made with the idea of first precipitating the manganese as manganese dioxide and thereby produce a precipitate which is free from manganese and colorless.

Method:

The solution used for this test was prepated by leaching an ore which had been roasted with sulphuric acid and was known to contain manganese. The sulphate and iron were precipitated as in the previous tests. Saturated chlorine water was then added to the solution and gaitated for several hours when the black precipitate was filtered off. The zinc was precipitated in the usual manner with lime.

Conclusions:

1. A precipitate can be obtained which is very white, containing very little manganese and less than one-half per cent iron.

2. While complete extraction in these tests was not obtained due to not enough lime, later tests with

sufficient lime showed no increase in the amount of manganese.

3. The test in which bleaching powder was used in hot solution gave good results as the precipitate was white and contained very little manganese and iron.

4. A good grade of precipitate was obtained which assayed 48 per cent zinc.

5. A comparatively large amount of zinc was retained by the precipitate obtained from the chlorine. This was largest in the heated solutions.

6. The elimination of manganese is not due to being removed from solution but rather to a highly oxidized condition of the manganese which prevents it being precipitated.

(Table 9)

Removal of Manganese
by the Use of Chlorine.
Table 9

No.	Vol	$CaSO_4$ Gm Zn	Cl Ppt Gm Zn	% Mn	Wt. Zn Ppt	% Zn	% Fe	% Mn
1	500	0.18	1.20	nil	13.9	49.0	0.36	0.09
2	"	0.11	0.34	2.40	12.7	51.7	0.46	0.06
3	"	0.11	0.72	6.30	15.4	46.7	0.44	0.05
4	"	0.38	0.86	1.20	15.2	48.5	0.43	0.13
5	"	0.55	3.00	0.53	13.8	46.0	0.45	0.24

No.	% CaO	% MgO	% Cl	Gm Zn	Sol. Gm Zn	Total Zn	Ext.
1	10.8	0.38	5.17	6.82	6.50	14.70	45.0
2	8.3	0.38	6.12	6.60	8.50	15.55	43.5
3	7.6	0.25	5.17	7.20	6.70	14.74	47.2
4	7.2	0.28	6.81	7.40	7.35	15.99	48.6
5	8.6	0.52	6.05	6.35	6.55	16.55	41.5

The original solution contained 30.5 gm Zinc per liter of solution.

#1 Hot Bleaching powder used, 20# per ton.

#2 200 cc saturated chlorine water per 500 cc solution.

#3 400 " " " " " " " "

#4 200 " hot " " " " " " "

#5 400 " " " " " " " " ".

Table 10.

Cyclic Leaching and Precipitation

No.	Sol Vol	Gm Zn	Gm Ppt	% Zn	Gm Zn	% Zn	% Fe	% Mn	% CaO	% MgO	% Cl
1	500	16.6	31.0	50.8	15.8		0.75	.207	2.31	nil	3.61
2	"	"	42.0	50.4	21.2		0.12	1.54	3.96	"	17.05
3	"	"	10.0	53.0	5.3		0.18	0.27	3.26	"	9.76
4	"	"	21.8	49.8	10.8		0.15	.208	4.60	"	7.45
5	"	"	27.0	51.0	13.8		0.28	.54	4.08	"	12.95
6	"	"	29.65	55.7	16.5		0.20	.234	2.32	"	11.00
7	"	"	20.30	53.60	10.9		0.23	.207	3.20	"	9.26
8	"	"	27.60	48.30	13.30		0.12	.055	7.17	"	8.42
9	"	"	22.70	45.00	10.2		.092	.134	5.76	"	7.05
10	"	21.6	54.60	52.0	26.4		.04	.268	4.87	"	10.60
11	"	21.6									
12	"	21.6									

214.2 grams of zinc in the solution precipitated.

Table 10

Cyclic Leaching and Precipitation.

No.	% SO_4	% Zn Calcine	% Zn Vol	Barren Sol cc	Barren sol %Zn	Barren Sol gm Zn	Wash cc	Wash % Zn	Wash gm Zn	Total gm Zn
1	7.7	67.1	7.3	450	0.25	1.12	100	1.62	1.62	18.54
2	11.65	65.1	11.05	400	0.05	0.20	138	0.82	1.14	22.54
3	5.70	67.5	7.90	480	0.15	0.72	102	0.87	0.89	6.86
4	12.50	62.8	5.80	360	0.115	0.417	250	0.785	1.96	13.18
5	4.69	65.2	9.45	430	0.10	0.43	124	0.95	1.18	15.41
6	3.08	71.4	6.90	600	0.05	0.30	173	1.00	1.73	18.53
7	7.95	67.6	3.05	575	0.30	1.72	157	0.75	1.18	13.81
8	10.40	58.4	3.00	207	0.125	0.32	210	0.58	1.22	14.84
9	13.70	63.7	2.00	550	0.30	1.65	210	0.62	1.30	13.15
10	12.30	64.5	7.50	1090	0.25	2.72	200	1.00	2.00	33.12
11				680	1.50	10.20				10.20
12				1215	2.40	29.16				29.16
							Total	Zinc		209.34

Summary of Results on
Cyclic Leaching and Precipitation

The ore used in this test was Bullion Coalition #13. The ore was first roasted in the usual way by adding one equivalent of sulphuric acid to the ore and roasting at a temperature of 700°C. for one hour. It was then leached with two volumes of water. This solution was then purified by first passing in chlorine gas and then adding powdered calcium carbonate and agitating for two hours. The chlorine gas served to oxidize the manganese and iron so that they would not contaminate the precipitate. The precipitate from this was then filtered and to the solution the required amount of calcium chloride added to remove the sulphate. The calcium sulphate was then filtered out.

Five hundred cc. of the above solution was taken for the first precipitation. Ninety per cent of the required amount of lime paste was added to the solution and then agitated for four hours. The precipitate was then allowed to settle and the clear solution drawn off. Five hundred cc. of fresh zinc chloride solution was then added, the solution agitated for four hours, allowed to settle, and the clear solution drawn off. Again, 500 cc. of fresh zinc chloride solution was added and the same procedure followed. This time the precipitate was filtered and washed, the wash water being kept separate from the other solutions.

The second solution to be drawn off from the above precipitation was the second solution to be precipitated. The required amount of lime paste was added and agitated for four hours. It was then settled and the solution drawn off and the third solution from the first precipitation added, agitated, settled, and drawn off. To the precipitate, fresh zinc chloride solution was added. This was agitated, settled, filtered and washed.

The second solution drawn from the second precipitation was the third solution to be precipitated. The same procedure was followed in this as in the other precipitations.

The barren solutions from the precipitations were analysed and together with the wash water were used to leach more ore. This solution was treated in the same way as the solution first used in this test. The purified solution was then used as the fresh zinc chloride for use on the precipitates. The barren solutions obtained after this were used in the same way to leach more ore and used as fresh solution in the cyclic process.

1. The reason for the high manganese in the second precipitate was because there was more than the required amount of lime added to the solution to precipitate the zinc.

2. In the eighth and ninth precipitates the lime is too high. This was due probably to the length of time of agitation being less than four hours.

3. The variation in the amount of chlorine is due to different degrees of washing. This could not be avoided in these tests as the surface of the precipitate cracks when it is being filtered.

4. The high sulphate in the precipitate is not accounted for.

5. A slight yellow color is found in the calcined precipitate. This probably would make it unsuitable for use as a pigment.

CONCLUSION

The work in this thesis has shown that the recovery of zinc by precipitation from solution is commercially possible. Lime is the best precipitant for this work. The difficult of removing manganese from the precipitate can be overcome by the use of a strong oxidizing agent as chlorine, either as the gas or generated from bleaching powder. In order to successfully operate a plant would need to be worked on the principle of counter-current decantation. This is necessary if lime which is present in too large amounts is to be removed.