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Method for Recovering Anhydrous $ZnCl_2$ From Aqueous Solutions

By B. R. Eichbaum and L. E. Schultze

UNITED STATES DEPARTMENT OF THE INTERIOR

MARCH 3, 1849

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	$\mu g/mL$	microgram per milliliter
g	gram	min	minute
g/L	gram per liter	mol	mole
h	hour	mol/L	mole per liter
hp	horsepower	pct	percent
in	inch	psig	pound (force) per square inch, gauge
L	liter	rpm	revolution per minute

METHOD FOR RECOVERING ANHYDROUS $ZnCl_2$ FROM AQUEOUS SOLUTIONS

By B. R. Eichbaum[1] and L. E. Schultze[2]

ABSTRACT

To develop technology to assure an ample supply of zinc and to reduce environmental pollution, the U.S. Bureau of Mines investigated alternatives to the roast-leach process for treating complex sulfide concentrates. Previous studies proved that low-grade zinc sulfide (ZnS) concentrates could be leached using chlorine-oxygen to produce zinc chloride ($ZnCl_2$). The process involves high energy requirements for evaporating the pregnant solution to produce anhydrous $ZnCl_2$ needed for electrolytic cell feed. An efficient hydrometallurgical process would facilitate treatment of lower grade ores than can be used in conventional processing and would render roasting unnecessary.

An alternative method was devised for recovering $ZnCl_2$ from solution. Zinc diammine chloride [$Zn(NH_3)_2Cl_2$] was precipitated from solution by adding ammonium chloride (NH_4Cl) and sparging with ammonia (NH_3) to a pH of 6 to 7.5. The spent solution was treated with calcium hydroxide [$Ca(OH)_2$] at 60° to 80° C for 1 to 4 h to remove remaining zinc and NH_3. The $Zn(NH_3)_2Cl_2$ was heated to 300° to 400° C to remove NH_3 and produce anhydrous $ZnCl_2$. A possible flowsheet was devised and is included.

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INTRODUCTION

At the present time, zinc is produced commercially by a roast-leach zinc electrowinning process (*1*).[3] The primary source is high-grade concentrates of the mineral ZnS. Concentrates must contain low levels of iron to avoid formation of zinc ferrites during roasting because zinc ferrites are not amenable to leaching and cause decreased zinc recovery. Also, SO_2 is produced during roasting and must be scrubbed from flue gases to prevent air pollution. Progressively more stringent standards for SO_2 emission and interest in processing more complex sulfide deposits have prompted research to develop hydrometallurgical processes as alternatives to the conventional roast-leach treatment of ZnS concentrates (*2-16*). Most complex sulfides are lower grade, contain more impurities, and are not amenable to treatment by existing techniques.

One method that shows promise is chlorine-oxygen leaching. This method is particularly well suited to treating ores that are high in iron content (*2*) and yields a concentrated $ZnCl_2$ solution. Metallic zinc may be recovered from the solution by electrowinning; however, it is of unsatisfactory quality. There are no known techniques for producing a satisfactory zinc plate from chloride solutions. As an alternative, a molten-zinc product can be produced by molten-salt electrolysis of anhydrous $ZnCl_2$ (*17-19*).

Molten-salt electrolysis of $ZnCl_2$ yields a molten-zinc product, which can be tapped from the cell in a continuous manner. Since the molten-salt cell operates at a temperature of 500° C, the $ZnCl_2$ feed must be anhydrous to avoid explosive release of steam. Also, the presence of O_2 will cause corrosion of the carbon electrodes.

Recovering anhydrous $ZnCl_2$ from aqueous leaching solutions has proven in the past to be an expensive, energy intensive, and difficult task. During evaporative crystallization, the high solubility of $ZnCl_2$ results in viscous mother liquors that are very difficult to filter. Additionally, while $ZnCl_2$ is easily dried, the anhydrous salt is deliquescent and maintenance of anhydrous conditions is difficult. Shanks (*18*) noted that some types of $ZnCl_2$, purchased as feed for molten-salt electrowinning studies, were less hygroscopic than others. Analysis indicated the presence of NH_3, suggesting the presence of a double salt or an ammine chloride. Development of an efficient method for producing a zinc-ammonia salt would yield a less deliquescent feed material for molten-salt electrolysis.

Previous studies by Kruesi (*20-21*) have shown that zinc-ammonia salts can be generated through solvent extraction techniques. $ZnCl_2$ is extracted from an aqueous solution into an organic phase and is then stripped into a solution from which an ammine chloride can be crystallized. Kruesi proposed two methods for stripping zinc from the organic phase. One method employed ethylene glycol and the other employed an aqueous ammoniacal chloride solution as the stripping solution (*20*). The ethylene glycol solution was contacted with gaseous ammonia to crystallize zinc ammine chloride followed by heating of the recovered precipitate to remove ammonia. To avoid contamination of the $ZnCl_2$ product by residual ethylene glycol, Kruesi recommended recrystallization of the zinc ammine chloride prior to thermal treatment. In the second method, the organic was stripped at elevated temperature (*21*). Zinc ammine chloride was crystallized from the stripping solution by cooling. The crystalline product was recovered by filtration; the mother liquor composition was adjusted by addition of ammonium hydroxide and was recycled to the stripping circuit.

If an ammoniacal $ZnCl_2$ salt could be precipitated directly from an aqueous leach solution, the solvent extraction step could be avoided. This would simplify the recovery sequence by avoiding either the need for recrystallization or concern over premature crystallization during solvent extraction. As part of its program to assure an adequate supply of metals and minerals from domestic sources, reduce environmental pollution, and conserve energy, this study was done to demonstrate technical feasibility for crystallization of an ammoniacal $ZnCl_2$ salt directly from an aqueous leach solution and conversion to anhydrous $ZnCl_2$. If solvent extraction can be avoided, there should be a cost savings in the process.

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[3] Italic numbers in parentheses refer to items in the list of references at the end of this report.

METHODS AND PROCEDURES

Solutions used in crystallization tests were prepared from reagent-grade salts by dissolving weighed quantities in deionized water. All chemicals added to promote crystallization were reagent grade. Spray drying tests were done in a minispray dryer. Precipitated products were recovered by vacuum filtration and dried at 110° C.

Ammonia sparging tests were performed in a 3-L water-jacketed borosilicate glass resin kettle having four standard taper joints in the lid (fig. 1). Temperature was controlled by a refrigerated circulating bath (minus 20° to plus 300° C) connected by rubber tubing to the sparging kettle water jacket. Temperature was monitored with a Chromel-Alumel[4] thermocouple and a digital temperature indicator.

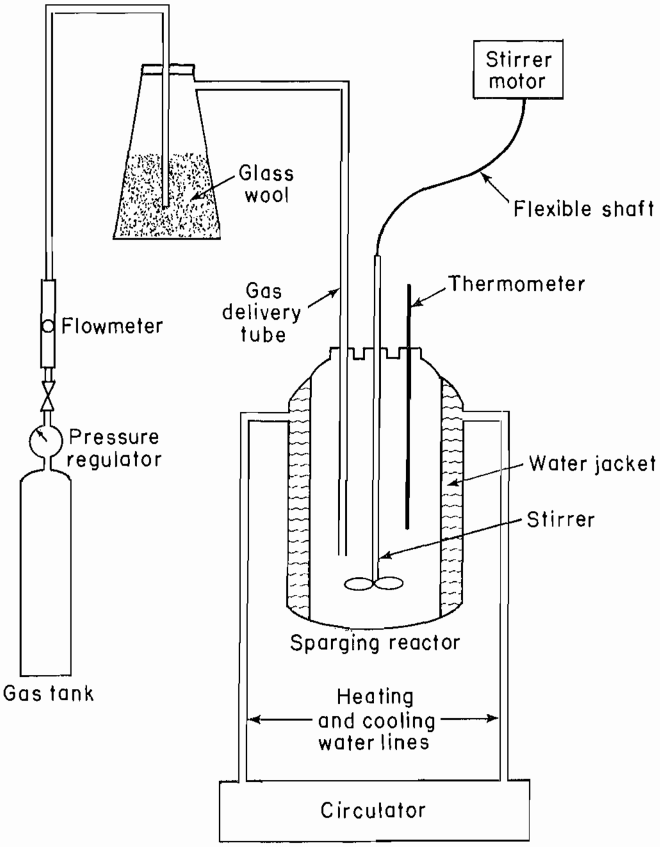

Figure 1.—Sparging apparatus.

Anhydrous NH_3 was delivered through a pressure regulator and flowmeter to a fritted glass tube located just above the propeller in the sparging vessel. The $ZnCl_2$ solution was stirred with a three-bladed, steel-reinforced polyethylene stirrer (18-in length, 1/4-in shaft diameter, 1-3/4-in propeller diameter, and 45° pitch) connected by a flexible shaft assembly to a variable speed 1/40-hp electric motor capable of 0- to 6,000-rpm armature shaft speed. A standard taper inlet adapter with a slightly oversized 1/4-in hole was used as the centering device and bushing for the stirrer. The bushing was not made gas tight to avoid pressure buildup in the system. The lime treatment was performed in 2-L beakers using magnetic stirring. The pH was monitored with a pH meter.

The chloride and NH_3 concentration in solutions and crystallized salts were obtained by wet chemical methods. Metal analyses were obtained by atomic absorption spectroscopy or inductively coupled plasma spectroscopy. Crystal structures of precipitates were determined by X-ray diffraction. O_2 content of precipitates was determined by inert gas fusion at the Bureau's Albany Research Center. Differential thermal analysis was done on ammoniacal salts to determine the temperatures at which ammonia could be removed.

Calcination tests were done in a 3-L resin kettle fitted with a heating mantle, and the vapors were vented through a scrubber (fig. 2). Temperature was controlled using a Chromel-Alumel thermocouple, located over a porcelain

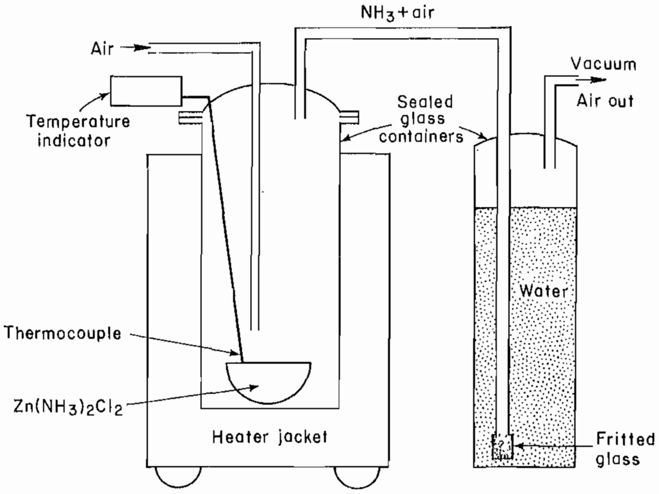

Figure 2.—Thermal decomposition apparatus.

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[4] Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

evaporating dish containing the sample. Two glass tubes were introduced through sealed, tapered joints in the lid of the resin kettle. One tube extended to just above the porcelain dish, providing outside air to sweep away reaction products. The second tube, near the top of the vessel, carried the reaction products to the scrubber. The scrubber consisted of a gas dispersion tube immersed in water, and the reactor was evacuated to draw reaction products from the calciner. Water from the scrubber was titrated for NH_3 content at the end of each test.

RESULTS AND DISCUSSION

SCREENING TESTS

Preliminary screening tests were done to determine the conditions under which ammoniacal $ZnCl_2$ salts could be formed. Crystalline products from the tests were used to obtain X-ray diffraction characterization and differential thermal characteristics.

The first technique investigated was one previously used to produce zinc ammine chloride (*20*) or magnesium ammine chloride (*22*). An aqueous solution of $ZnCl_2$ was dissolved in ethylene glycol and sparged with NH_3 at 20° C. Solution progressed from colorless to milky white as sparging progressed and crystallization commenced. Separation of crystals from the ethylene glycol solution was difficult because solution viscosity and filtered crystals contained entrained organic material. Analysis of crystalline products showed that $Zn(NH_3)_2Cl_2$ was the major product with some amorphous material and a trace of $ZnCl_2 \cdot 2NH_4Cl$.

Formation by evaporative crystallization was another method evaluated. To test the feasibility of this approach, 1 mol/L $ZnCl_2$ solutions were oven evaporated under different conditions (table 1). When $ZnCl_2$ solutions were evaporated, a contaminant appeared in the product. The contaminant had a distinct but unknown X-ray diffraction pattern. Adding 1 mol/L NH_4Cl to the test solutions produced an NH_4Cl double salt plus hydroxychloride under atmospheric conditions and zinc oxide (ZnO) with a trace of the double salt when dried under vacuum. In tests using a spray dryer, no crystals were produced by aspirating $ZnCl_2$ solution with air in an attempt to produce $ZnCl_2$ crystals (table 2). Aspirating a solution of $ZnCl_2$ and NH_4Cl with air produced a mixture of double salts and amorphous material. Aspirating either solution with ammonia produced zinc ammine chloride. Some additional tests were done using $ZnCl_2$ recovered from solution by vacuum drying. The recovered salts were exposed to an NH_3 atmosphere for 1 h at 20° C. Part of the $ZnCl_2$ was converted to $(NH_4)_2ZnCl_4$. The converted material was ground to minus 200 mesh and again exposed to an NH_3 atmosphere for 1 h at 20° C. The final product was $Zn(NH_3)_2Cl_2$.

Table 1.—Evaporative drying of $ZnCl_2$ solutions

Test solution and drying process	Product
$ZnCl_2$:	
70° C, 60 days	$ZnCl_2$, unk.
150° C, 8 days (vacuum)	$ZnCl_2$, unk.
$ZnCl_2$, NH_4Cl:	
70° C, 12 h	$ZnCl_2 \cdot 2NH_4Cl$, $Zn(OH)_8Cl_2$.
150° C, 12 h (vacuum)	ZnO, m-unk, t-$ZnCl_2 \cdot 2NH_4Cl$.

m Minor. t Trace. unk Unknown.

Table 2.—Spray drying $ZnCl_2$ solutions

Carrier gas and test solution	Temp, °C	Product
Air:		
$ZnCl_2$	100	No powder (wet slurry).
$ZnCl_2$, NH_4Cl	115	$ZnCl_2 \cdot 2NH_4Cl$, (m-amorphous, t-$ZnCl_2 \cdot 3NH_4Cl$).
NH_3:		
$ZnCl_2$	120	$Zn(NH_3)_2Cl_2$.
$ZnCl_2$, NH_4Cl	115	$Zn(NH_3)_2Cl_2$, NH_4Cl.

m Minor. t Trace.

Preliminary tests were also performed to crystallize zinc ammine salts directly from solution by titrating 1 mol/L $ZnCl_2$ solution with NH_4OH. Tests done at ambient temperature produced ZnO with minor $Zn(NH_3)_2Cl_2$ at pH 7.0. Repeating the test at 60° C yielded ZnO and two unidentified phases at pH 6.2. Titrating a mixture of $ZnCl_2$ and NH_4Cl at ambient temperature yielded different crystalline products as pH increased from 6 to 8 (table 3). Oxychlorides were the major products, up to pH 6.5, and were present at all pH levels tested.

Having found that at least three different zinc ammine salts may be crystallized from $ZnCl_2$ solutions, it became important to determine whether any of the three would be more desirable as feed to the fused-salt electrolysis cell. To this end, differential thermal analysis was done on each salt (figs. 3-4). The broad endothermic peak shown for each salt indicates loss of ammonia, while a second heating cycle showed only endothermic peaks at temperatures

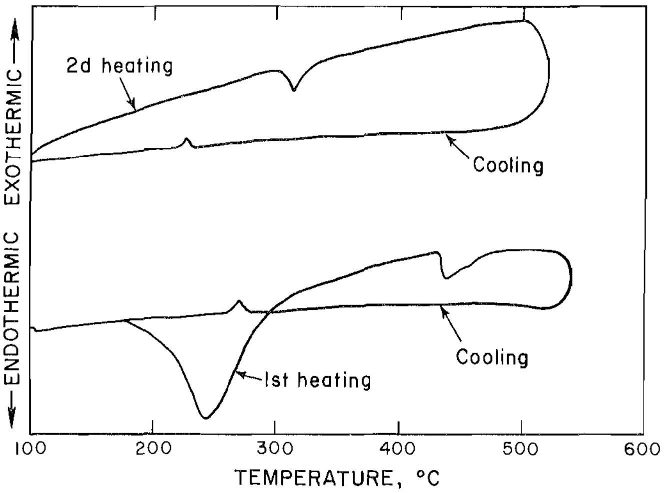

Figure 3.—Differential thermal analysis of $Zn(NH_3)_2Cl_2$.

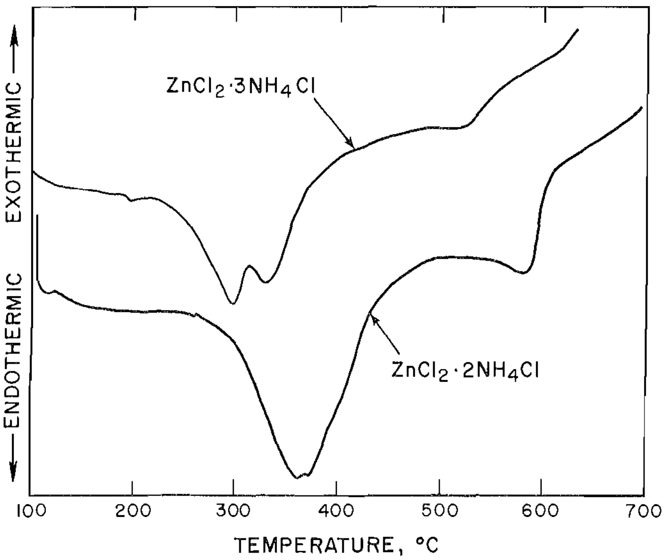

Figure 4.—Differential thermal analysis of $ZnCl_2 \cdot NH_4Cl$ double salts.

corresponding to melting and boiling of $ZnCl_2$. Ammonia removed from $ZnCl_2 \cdot 2NH_4Cl$ and $ZnCl_2 \cdot 3NH_4Cl$ was in the form of NH_4Cl, which deposited as a white film on any cool surface. It was felt that recovery of ammonia as NH_4Cl using the two double salts would complicate a continuous process; therefore, further research was concentrated on crystallizing $Zn(NH_3)_2Cl_2$, from which NH_3 is recovered as a gas.

Table 3.—NH_4OH titration of $ZnCl_2 \cdot NH_4Cl$ solutions

Solution pH	*Product*
6	$Zn_5(OH)_8Cl_2$, m-$Zn(NH_3)_2Cl_2$, m-$ZnCl_2 \cdot 2NH_4Cl$.
6.5	$Zn_5(OH)_8Cl_2$, m-$Zn(NH_3)_2Cl_2$, t-$ZnCl_2 \cdot 2NH_4Cl$.
7.0	$Zn(NH_3)_2Cl_2$, t-$Zn_5(OH)_8Cl_2$, t-$ZnCl_2 \cdot 2NH_4Cl$, t-unk.
7.3	$Zn(NH_3)_2Cl_2$, m-unk, t-$Zn_5(OH)_8Cl_2$.
7.5	$Zn(NH_3)_2Cl_2$, unk, t-$Zn_5(OH)_8Cl_2$.
8.0	$Zn(NH_3)_2Cl_2$, unk, t-$Zn_5(OH)_8Cl_2$.

m Minor. t Trace. unk Unknown.

SPARGING TESTS

Since the ammine chloride was formed both by spray drying using NH_3 carrier and by precipitation using NH_4OH, it was likely that it could also be formed by sparging a $ZnCl_2$ solution with gaseous NH_3. Such an approach has the advantages of crystallizing a zinc product directly from solution, avoiding the costly water removal required by evaporative techniques, and facilitating the recovery of NH_3 gas for recycle. To avoid excess use of NH_3, it was necessary to determine the minimum time required for sparging to reach completion. A convenient way to determine this was to do a series of tests to measure the effect of pH on $Zn(NH_3)_2Cl_2$ solubility, which established minimum solubility of the salt.

A $Zn(NH_3)_2Cl_2$ crystalline product (38 pct Zn) from previous tests was used. When $Zn(NH_3)_2Cl_2$ was added to deionized water, the pH rose from 4.0 to 7.5 and 0.25 g/L Zn dissolved in solution (fig. 5). Solution samples were taken at different pH values and analyzed for zinc content. When NH_4OH was added to the solution to raise the pH to 8.3, the zinc in solution decreased to 81 μg/mL. With continued increase of pH, zinc in solution increased from 0.19 g/L at a pH of 9.0 to 5.6 g/L at a pH of 11.4 where all the crystals were dissolved.

To obtain information at lower pH values, HCl was added to a saturated solution of $Zn(NH_3)_2Cl_2$. Zinc in solution increased from 0.285 g/L at a pH of 7.5 to 3.1 g/L at a pH of 6.7. Continued addition of HCl did not decrease solution pH, but continued to dissolve zinc until all of the $Zn(NH_3)_2Cl_2$ had gone into solution. From these results, it appeared that sparging to a pH range of 7.5 to 9.0 would precipitate most of the zinc. A pH of 8.3 would be desirable.

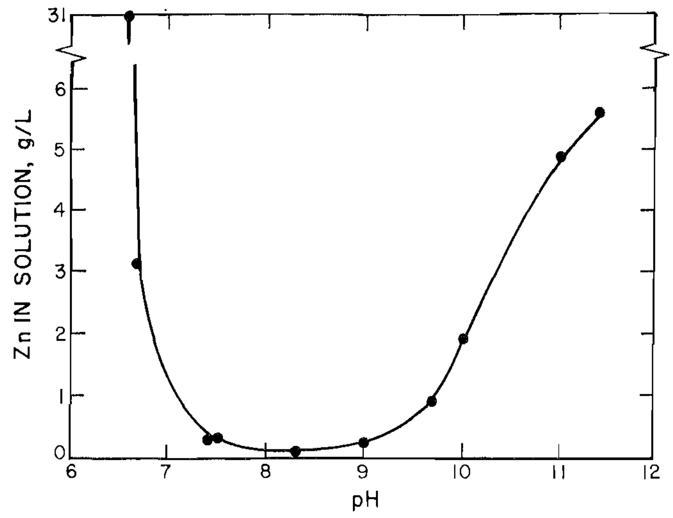

Figure 5.—Effect of pH on solubility of $Zn(NH_3)_2Cl_2$.

Initial NH_3 sparging tests were done on 2-L samples of 1 mol/L $ZnCl_2$ at 20° C. Samples of crystalline products were taken as the test progressed and the pH was recorded. Analysis of the products showed that most of the precipitate was ZnO, an undesirable feed for a molten-salt electrolysis cell. It was observed, however, that continued sparging dissolved all of the precipitate. By acidification of the solution containing dissolved ZnO to pH 7.2 with gaseous HCl, $Zn(NH_3)_2Cl_2$ was precipitated as the major product. Because large quantities of NH_3 and HCl are consumed using this method, tests were done adding NH_4Cl to the $ZnCl_2$ solution to obtain the same result.

A series of tests was done at 20° C, starting with 1 mol/L $ZnCl_2$ containing NH_4Cl at zinc-to-NH_3 molar ratios of 1:0 to 1:7. Tests were considered complete when no additional crystallization from solution could be noted as more NH_3 was sparged and pH increased. The compositions of the initial solution and final filtrates were determined as were the compositions of crystalline products (table 4). Evaluation of results showed that ZnO was a major product until the initial $ZnCl_2$-to-NH_4Cl molar ratio exceeded 1. In the test at a ratio of 1:0 $ZnCl_2$:NH_4Cl, zinc concentration in the final solution is higher than predicted from figure 5 data. The presence of ZnO in the precipitate indicates that some of the $ZnCl_2$ was hydrolyzed and NH_4Cl was generated. From the results of the tests, it is apparent that the presence of NH_4Cl in the starting solution increases zinc solubility. Some ZnO was still detected when the $ZnCl_2$-to-NH_4Cl ratio was 1:2, but O_2 analysis was 2.9 pct, a level considered acceptable for feed to a fused-salt electrolysis cell. Larger ratios of NH_4Cl lowered O_2 content to 1.1 pct. The value of 2.7 pct for the ratio of 1:6 is thought to be due to incomplete drying of the sample prior to analysis. Thus, O_2 content is high because of the presence of H_2O. For the ratio of 2 mol NH_4Cl per 1 mol $ZnCl_2$, which is the minimum needed to reduce O_2 content to an acceptable level, 15 pct of the zinc will remain in sparging mother liquors containing 2.3 mol/L NH_4Cl. The sparging mother liquor will need to either be treated for NH_4Cl recovery or recycled to leaching to avoid unacceptable reagent consumption.

If the mother liquors are recycled to a Cl_2-O_2 leach, there is concern that NH_4Cl would be lost by decomposition to N_2 and H_2. If inhibition of ZnO species was due to increased chloride concentrations, using a more stable chloride salt could provide the concentrations required to control O_2 levels. To study the effectiveness of a more stable salt, tests were done in which NH_4Cl was replaced with calcium chloride ($CaCl_2$) and mixtures of $CaCl_2$ and NH_4Cl. Use of $CaCl_2$ yielded crystalline products of ZnO salts. The $CaCl_2$-NH_4Cl mixtures yielded $Zn(NH_3)_2Cl_2$, along with $ZnCl_2 \cdot 2NH_4Cl$, ZnO, and amorphous phases. As the substitutions for NH_4Cl were not effective, all further tests employed NH_4Cl.

EFFECT OF IMPURITIES

Having demonstrated a technique for crystallization of $Zn(NH_3)_2Cl_2$ directly from aqueous solutions of $ZnCl_2$, attention turned to the distribution of potential impurities in actual leaching solutions. A simulated leaching solution was prepared based on the composition stated in earlier work (*2*). The solution contained, in grams per liter: 97 Zn, 4.5 Fe, 2.0 Cu, 1.0 Ca, 0.15 Cd, 0.11 Ni, 0.022 Pb, and 0.041 Co. The pH was 4.2. Sparging up to pH 5.6 resulted in amorphous precipitates containing all of the copper and iron. Above pH 5.6, zinc ammine chlorides were obtained, which, when analyzed by X-ray fluorescence spectroscopy, contained no impurities. The results indicate that the major contaminating impurities could be removed by adjusting the solution pH to 4 to 5, thus precipitating iron and copper prior to crystallizing $Zn(NH_3)_2Cl_2$.

Since hydrous ferric oxide is formed during sparging and is known to act as a collector for other metal ions, additional tests were done on simulated leaching solutions containing no iron to determine whether copper contamination would still occur. Precipitates were removed at intermediate pH values and analyzed (table 5). The results show that copper precipitates below pH 6.3 as a hydroxychloride, but redissolves at higher pH to yield uncontaminated $Zn(NH_3)_2Cl_2$. Thus, the sparging technique may be used to recover and purify zinc from aqueous solutions. If iron is present, it must be removed in a separate step. Solution analyses indicate that impurities such as calcium, cadmium, cobalt, and nickel remain in sparged mother liquors and, therefore, would not contaminate crystallized products.

Table 4.—NH_3 sparging of $ZNCl_2 \cdot NH_4Cl$ solutions

$ZnCl_2$:NH_4Cl molar ratio in water	Final pH	Solution content, g/L						Crystalline precipitate			
		Zn		NH_3		Cl		X-ray product	NH_3, pct	Cl, pct	O_2, pct
		S	F	S	F	S	F				
1:0	7.6	60	25	0.0	40.0	73.7	62.5	ZnO, $Zn(NH_3)_2Cl_2$	11.7	28.7	10.8
1:0.5	6.9	60	12	8.2	34.9	83.2	76.6	ZnO, $Zn(NH_3)_2Cl_2$, t-unk	7.7	29.6	7.2
1:1	6.7	60	20	16.8	45.8	96.8	82.7	ZnO, $Zn(NH_3)_2Cl_2$	10.2	28.1	9.2
1:1.5	6.6	60	15	19.9	39.5	112.5	87.7	$Zn(NH_3)_2Cl_2$, m-ZnO	13.5	34.8	5.1
1:2	6.4	60	8.7	27.9	38.9	127.0	80.0	$Zn(NH_3)_2Cl_2$, t-ZnO	16.6	39.2	2.9
1:4	6.3	60	9.6	56.3	65.2	174.2	129.7	$Zn(NH_3)_2Cl_2$, pos t-$ZnCl_2 \cdot 2NH_4Cl$	15.8	41.9	1.6
1:6	6.2	60	7.3	78.1	86.3	211.2	176.7	$Zn(NH_3)_2Cl_2$, t-$ZnCl_2 \cdot 2NH_4Cl$	17.8	42.1	2.7
1:7	6.0	60	14	80.8	98.5	215.2	208.7	$Zn(NH_3)_2Cl_2$	18.4	42.6	1.1

F Crystalline products after NH_3 sparging.
m Minor.
pos t Possible trace.
S Starting solution.
t Trace.
unk Unknown.

Table 5.—Distribution of impurities during sparging crystallization of $Zn(NH_3)_2Cl_2$

pH	Crystalline product	Crystalline content, pct			Solution content, µg/mL					
		Zn	Cl	Cu	Zn	Cu	Ca	Co	Cd	Ni
4.0	NAp	NAp	NAp	NAp	68	970	900	33	220	49
6.3	$Zn(NH_3)_2Cl_2$, m-$ZnCl_2 \cdot 2NH_4Cl$ $CuCl_3 \cdot 3[Cu(OH)_2]$	35	25	15	71	180	870	28	200	42
6.5	$Zn(NH_3)_2Cl_2$	40	35	ND	43	400	870	25	200	39
7.1	$Zn(NH_3)_2Cl_2$	40	40	ND	15	670	880	28	200	42
7.6	$Zn(NH_3)_2Cl_2$	40	35	ND	17	710	850	30	190	47
9.5	NAp	NAp	NAp	NAp	22	710	870	30	190	47

m Minor.
NAp Not applicable.
ND Not detected.

LIME TREATMENT OF MOTHER LIQUOR

While results of sparging tests confirmed that $Zn(NH_3)_2Cl_2$ could be crystallized from solution, the need to add NH_4Cl yielded mother liquors containing up to 15 pct of the initial zinc and large amounts of NH_4Cl. Recycling of the mother liquor to leaching would recover the zinc, but it was feared that the leaching conditions would decompose the NH_4Cl. Additions of $Ca(OH)_2$ to the mother liquors would convert NH_4Cl to $CaCl_2$, which would be compatible with Cl_2-O_2 leaching conditions and allow NH_3 to be recovered as a gas. Tests were done in which $Ca(OH)_2$ was added to a sparging mother liquor at 25°, 65°, and 80° C for a period up to 6 h to determine conditions for recovering NH_3. Since $Ca(OH)_2$ addition also precipitates zinc, its behavior was also monitored.

Figure 6 shows the decrease in ammonia content versus time for the three temperatures for a $Ca(OH)_2$ addition of 280 g/L of mother liquor. The addition level of $Ca(OH)_2$ was calculated as being sufficient for conversion of all of the NH_4Cl to $CaCl_2$ and all of the $ZnCl_2$ to ZnO. Zinc behavior is shown in figure 7.

At 25° C, the NH_3 decreased from 66.5 to 12.7 g/L and the zinc content decreased from 17 to 3.4 g/L in 320 min. At 65° C, the NH_3 decreased to 4.1 g/L and the zinc content decreased to 190 µg/mL in 260 min. At 80° C, the NH_3 decreased to 0.29 g/L and the zinc content decreased to 43 µg/mL in 160 min. Higher temperature not only decreased the amounts of both NH_3 and zinc, but yielded faster reaction times. The rapid decrease in both NH_3 and zinc concentrations at 80° C suggested that less $Ca(OH)_2$ may be required.

Tests using 210 and 140 g $Ca(OH)_2$ at 80° C yielded almost identical results to those shown in figures 6 and 7. Additions of 70 g $Ca(OH)_2$ yielded lower removal of both zinc and NH_3. A more detailed study of $Ca(OH)_2$ additions was not done at this time because analysis of precipitated material showed that $CaCO_3$ was present. Since fresh reagent-grade $Ca(OH)_2$ had been used, any carbonate apparently resulted from absorption of CO_2 from air by the ammoniacal solutions. Such absorption would be variable and uncontrolled so that the amount of added $Ca(OH)_2$ available for reaction with NH_4Cl could not be accurately measured. Age of solutions would, therefore, be a factor in $Ca(OH)_2$ requirements.

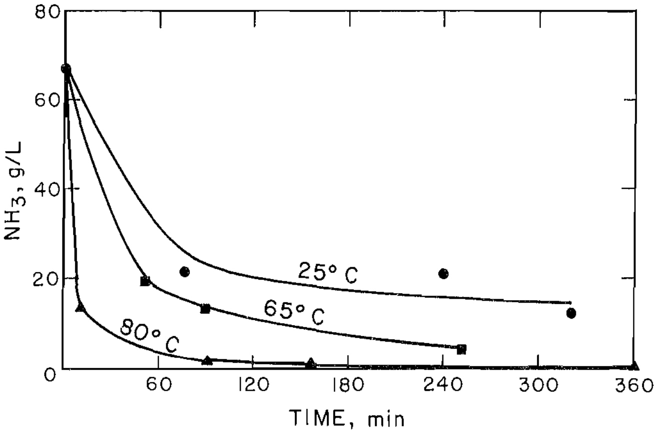

Figure 6.—Effect of time and temperature on ammonia removal from sparged mother liquors after adding 280 g/L $Ca(OH)_2$.

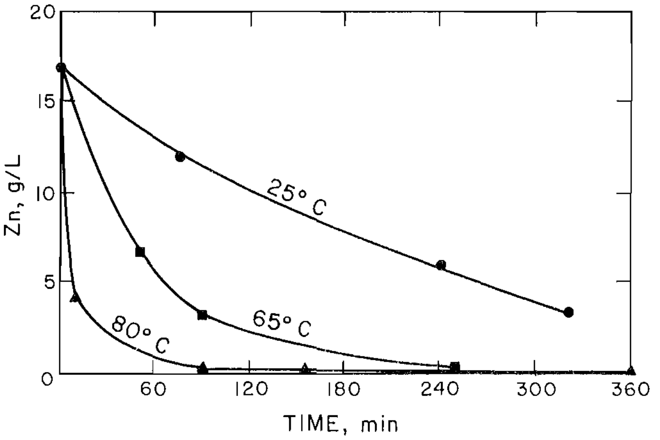

Figure 7.—Effect of time and temperature on zinc precipitation from sparged mother liquors after adding 280 g/L $Ca(OH)_2$.

THERMAL DECOMPOSITION OF $Zn(NH_3)_2Cl_2$

For $Zn(NH_3)_2Cl_2$ to be a practical intermediate for recovering anhydrous $ZnCl_2$ from solution, it must be possible to remove and recover the NH_3. To define the decomposition step and feasibility of producing NH_3 for recycle, tests were done over a range of temperatures and times (table 6). Ammonia removal was based on weight loss versus the calculated weight of NH_3 in the sample. Ammonia recovery was based on NH_3 reporting to the trap versus weight loss.

Table 6.—Thermal decomposition of $Zn(NH_3)_2Cl_2$

Temp, °C	Time, h	NH_3, pct Removed	NH_3, pct Recovered
250	5	62.5	89.4
275	2	55.6	93.4
300	2	102	97.8
300	3	85.4	97.8
300	4.5	105	95.4
300	5	99.1	97.4
325	3	96.1	92.9
325	5	99.2	92.9
350	1	102	94.5
350	1	49.5	91.7
350	2	101	82.4
375	4	103	97.1
400	1	107	55.7
400	4	105	67.2
450	1	115	67.5

While there is some variability in the NH_3 removal results, certain trends are apparent. At temperatures less than 300° C, the weight loss shows that NH_3 was incompletely removed, but most of the liberated NH_3 was recovered. At temperatures of 300° to 375° C, most of the tests resulted in near complete NH_3 liberation and recovery. At temperatures of 400° to 450° C, NH_3 was liberated, but recovery was incomplete. At the elevated temperatures, low NH_3 recovery was attributed to decomposition of NH_3 to N_2 and H_2. Confirmatory evidence for NH_3 decomposition was obtained by testing gas mixtures with a sensor to detect explosive mixtures. Explosive mixtures were detected for tests at 400° to 500° C, but not at lower temperatures. While NH_3 may form an explosive mixture, 16 pct NH_3 is required as opposed to 4.1 pct for H_2.

The major inconsistency in the data was the replicate test at 350° C for 1 h. The test in which 49.5 pct of the NH_3 was liberated was done on a charge that contained 58.6 pct more material and was the largest sample tested. The results were included to demonstrate that heat transfer in the salt is an important parameter for NH_3 liberation.

PROCESS FLOWSHEET

To illustrate how the $ZnCl_2$ recovery steps discussed in this report could be used as part of a zinc recovery process, a conceptual flowsheet developed from earlier work (*2*) was modified to include the NH_3 sparging treatment steps (fig. 8). Although the modification replaced the $ZnCl_2$ crystallization step with three separate operations, the new flowsheet offers several advantages. Foremost among the advantages is that the difficult and costly evaporative crystallization step is eliminated. Additionally, while the zinc cementation from the original flowsheet was retained, the investigation of the effect of impurities on $Zn(NH_3)_2Cl_2$ recovery demonstrated that it may be possible to eliminate this step unless recovery of those metals precipitated by zinc is desirable or unless such impurities build up to undesirable levels during recycle.

Inspection of the flowsheet shows a reasonably closed processing sequence in which the consumed reagents are lime, O_2, H_2S, and HCl. A potential buildup of $CaCl_2$ must be considered and could be handled by a bleedstream from the recycled $CaCl_2$ solution. Most of the added calcium would report to the residue as $CaSO_4$ produced in the reactor. Buildup of impurities, such as copper, cadmium, and nickel could also be controlled by a bleedstream. The metals could be recovered by zinc cementation of the bleedstream in a manner similar to the method described in earlier work (*2*). All aqueous streams are treated and recycled so that the only water losses from the process would be wash water in the leached residue.

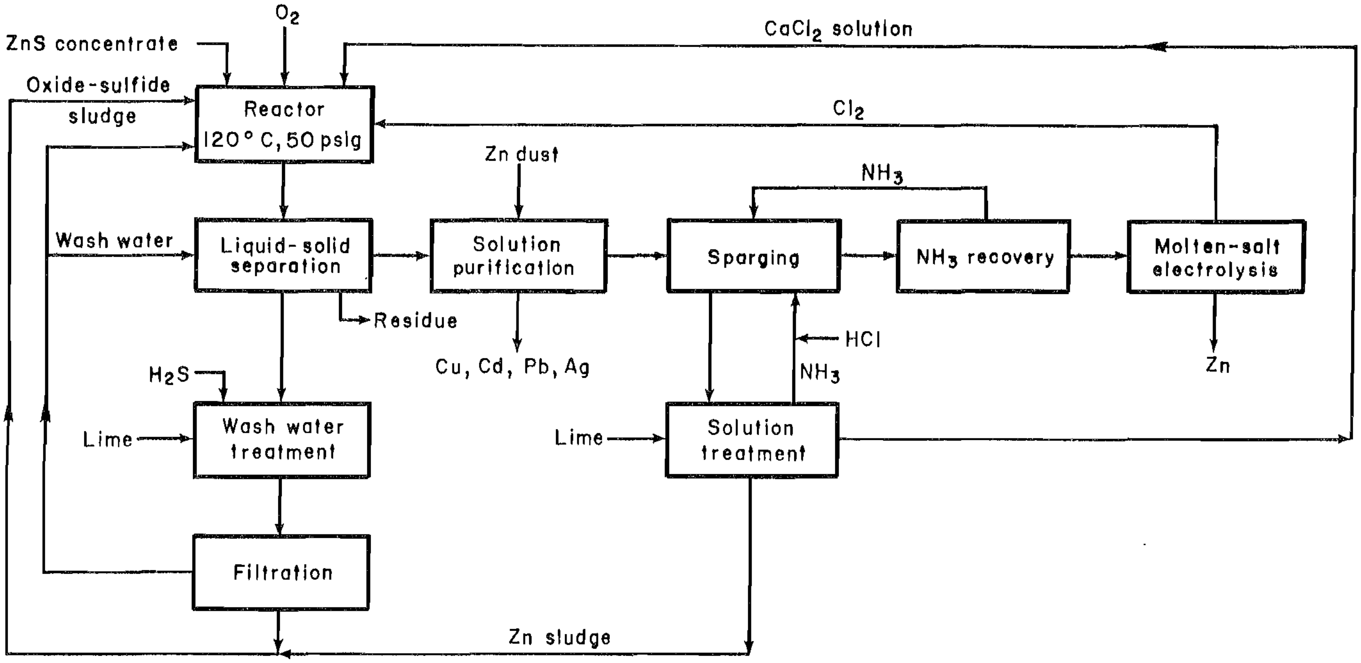

Figure 8.—Flowsheet for potential zinc recovery.

CONCLUSIONS

This investigation has demonstrated that $Zn(NH_3)_2Cl_2$ can be made from $ZnCl_2$ solutions or ZnS leaching solutions containing other metallic ingredients, by adding NH_4Cl to the solution and sparging with NH_3 to a pH of 6 to 7.5 at 20° C. After the zinc ammine chloride is precipitated from solution, the spent liquor can be reacted with $Ca(OH)_2$ to remove remaining zinc and NH_3 from solution. The $Zn(NH_3)_2Cl_2$ can be heated from 300° to 375° C for 1 to 4 h to drive off the NH_3 for recycling, and the $ZnCl_2$ can be used as feed to a fused-salt electrolysis cell.

The $ZnCl_2$ recovery technique resolves some of the difficulties encountered in recovering zinc from ZnS concentrates by chlorine-oxygen leaching. The need to concentrate leaching solutions by evaporation is eliminated and an easily filterable, crystalline precipitate is produced. The $Zn(NH_3)_2Cl_2$ precipitate is less deliquescent than $ZnCl_2$, which would facilitate storage of salts intended to be used as feed to a fused-salt electrolysis cell, thus increasing operating flexibility in the leaching system.

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