GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT INITIATION

Date: March 12, 1969

Project Title: Zinc Oxide Recovery Process

Project No.: A-1153

Project Director: W. H. Burrows

Sponsor: Kerr-McGee Chemical Corporation

Effective . . . . . . March 10, 1969 . . . . Estimated to run until: . . September 9, 1969 . . . .

Type Agreement: . . . . Industrial Research Agreement . . . . Amount: $ 8,760.00 . . . .

Reports: Monthly Progress Report (Report to include copies of daily notebook records.)
Final - Upon completion

Contact Person: Dr. L. E. Craig
Vice-President, Manufacturing
Kerr-McGee Chemical Corporation
Oklahoma City, Oklahoma 73102

Assigned to . . . . . CSMD . . . . Division

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B-4-28

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT TERMINATION

Date ____________________

PROJECT TITLE: Zinc Oxide Recovery Process

PROJECT NO: A-1153

PROJECT DIRECTOR: W. H. Burrows

SPONSOR: Kerr-McGee Chemical Corporation

TERMINATION EFFECTIVE: September 9, 1969

CHARGES SHOULD CLEAR ACCOUNTING BY: All charges have cleared.

Final Report Submitted 9-4-69

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Form EES 402 (R10-62)

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION

225 North Avenue, Northwest · Atlanta, Georgia 30332

April 1, 1969

Kerr-McGee Chemical Corporation
Kerr-McGee Building
Oklahoma City, Oklahoma 73102

Attention: Mr. L. E. Craig
Vice President - Manufacturing

Subject: Monthly Report. Project A-1153
Zinc Oxide Recovery Process
For the period, March 10 through March 31, 1969

Gentlemen:

Upon receipt of authorization from you to proceed with the research program outlined in the Work Statement of our proposal, and in consideration of the necessary delays required for procurement and installation of equipment for the pilot plant study, we have directed our efforts for the subject period to the laboratory studies listed in our proposal, as follows:

Experimental Program, Laboratory: Laboratory studies shall be made of the following factors, as they apply to the proposed process:

1. Crystal habit, particle size distribution and chemical composition of ZnO obtained in this process and its modifications.
2. Composition of the residue (iron oxide) from this process (under each modification), except that this study shall be included only in the event that funds remain after completion of the other studies.
3. Phase relationships of the system: $ZnO-NH_4Cl-NH_4OH-H_2O$. This study will be needed for two purposes: to enhance the possibilities of obtaining patent protection, and to reveal possibilities for process improvement.
4. Preliminary evaluation of chemical resistance of materials for construction of plant.

Our attention has been directed primarily to item 3, since this item has most immediate bearing upon the conduct of the pilot plant operation. Zerox copies of our notebook pages for this period are attached, showing the experiments performed and the results obtained. Of particular interest is the plot of experimental data shown on page 7, for the cross-over of curves for successive levels of ammonium chloride concentration was entirely unexpected. We have, nevertheless, verified these data points with subsequent experiments, and are confident of their accuracy.

The very steep slope of the 30g/100ml curve (as compared to the 25g/100 ml curve, for instance), indicates that this level of ammonium chloride loading would provide a much more efficient solvent for the extraction process than would the lower levels. Above the 30g/100ml level, however, we begin to encounter the possibility of ammonium chloride precipitating out with the zinc oxide. The curves on page 13 indicate that the slope of this curve, over the range of 60 to 80° C might be further increased by the addition of 4 ml conc NH_4OH per 100 ml solution, but would be decreased by the addition of 8 ml. It is anticipated that these conclusions will be tested in the pilot plant operation at a later date.

With reference to Item 4 of the Experimental Program, Laboratory, we have been in communication with International Nickel Company and are attaching copies of our correspondence with reference to evaluation of certain alloys. If you agree that this testing program would be appropriate as a portion of our Item 4 study, we shall follow up on this matter with International Nickel.

During April, we expect to complete Items 1 and 3 of the laboratory studies.

Respectfully submitted,

[redacted]

W. H. Burrows
Project Director

WHB:sm

2 enclosures

GEORGIA INSTITUTE OF TECHNOLOGY
STATE ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

RESEARCH RECORD BOOK No. 2591

RESEARCH PROJECT No. A-1153

ISSUED TO: Luis A. Garcia

DATE ASSIGNED: 3-12-69

DATE RETURNED: ____________

LABORATORY NOTEBOOK

No. 1

Mar. 12, 1969 thru

Project No. A-1153
for
KERR-McGEE CHEM. CORP
by
W. H. Burrows.
Project Director

Laboratory Task Assignments

1. Study of the phase relationships of the system $ZnO-NH_4Cl-H_2O$ at specified temperatures.
2. Study of the above with added NH_4OH
3. Study of the extraction of ZnO from steel furnace flue dust.

March 12, 69

Study of the phase relationship, $ZnO - NH_4Cl - H_2O$

Apparatus needed:

3-neck boiling flask equipped with condenser, stirrer and cap for removing aliquots.

Stirrer motor, thermometer, regulated-temperature water bath.

Preparation of reagents for the quantitative determination of ZnO by the Potassium ferrocyanide test. (procedure in page 4)

PROCEDURE:

NH_4Cl solution is prepared by dissolving the proper quantity in 200 ml. H_2O, and placing it in a 250 ml flask.

Addition of sufficient ZnO to saturate the soln. and stirring for about 20 min. - 40 min. is nessc. in order to have the solution in equilibrium.

Aliquots are taken after the motor has been stopped for few minutes and the solution is clear. A pre-heated pipette is used to get the samples. (about 10cc).

The amount of ZnO dissolved is determined by the method described on page 4.

3/12/69 W. H. Burrows

Factor = wt Zinc / ml $K_4Fe(CN)$ = $\frac{0.2}{ml\ K_4Fe(CN)}$

Snell & Biffen

sodium carbonate to complete neutralization and about 1 gram excess. Boil for 10 to 15 minutes. Wash off the watch glass, and allow the precipitated lead carbonate to settle. Filter the solution, and wash the precipitate by decantation, saving the washings. Pour about 10 ml. of 1:1 hydrochloric acid through the filter paper into the beaker containing the precipitate, so that it is completely redissolved. Cover the beaker, and reprecipitate with sodium carbonate. Filter through the same filter paper into the same receiving beaker, and wash well with hot water. Acidify the combined filtrates with 1:1 hydrochloric acid, adding 1 ml. excess. Boil to expel the bromine, and to the boiling solution slowly add 15 ml. of boiling 10 per cent barium chloride solution. Let stand for at least 1 hour on a steam bath, and filter through a weighed Gooch crucible or a retentive filter paper. Wash well with hot water, dry, and ignite carefully. Cool and weigh the barium sulfate, which is equivalent to the lead sulfate in the sample.

Calculation.

$$\text{Weight of barium sulfate} \times 1.299 \times \frac{100}{\text{weight of sample}} = \text{per cent lead sulfate}$$

Calculate the lead sulfate to lead oxide, and subtract from the total lead as lead oxide to give the amount present as oxide.

Per cent lead sulfate × 0.7360 = per cent lead sulfate as lead oxide
Total lead oxide − lead sulfate as lead oxide = lead oxide in sample

The sum of lead sulfate and lead oxide as such is the basic lead sulfate, subject to the usual amount of added zinc oxide.

Zinc as Zinc Oxide. Accurately weigh about 1 gram of pigment into a 400-ml. beaker, add 30 ml. of 1:2 hydrochloric acid solution, and boil for 2 to 3 minutes. Add 200 ml. of water, and make slightly alkaline with 1:1 ammonium hydroxide. Then make just acid with 1:2 hydrochloric acid. Add 3 ml. excess of the hydrochloric acid. Heat to boiling, and titrate with standard potassium ferrocyanide solution as described for the zinc oxide determination in the next method. Calculate as zinc oxide.

The sum of basic lead sulfate, zinc oxide, and insoluble matter should approximate 100 per cent. If the insoluble matter is substantial, it should be separately analyzed by the methods of Chap. 10 and reported by composition rather than as insoluble matter.

Zinc Oxide. **Zinc Volumetrically by Ferrocyanide.** The standard solution must first be prepared. Dissolve 22 grams of potassium ferrocyanide in water, and dilute to 1 liter. Each milliliter will be equivalent to about 0.005 gram of zinc, but the purity of the salt is such as to require standardization. Weigh about 0.2 gram of pure zinc or pure zinc oxide into a 400-ml. beaker. Dissolve in 30 ml. of 1:2 hydrochloric acid; then render just alkaline with 1:1 ammonium hydroxide. Make just acid with

5

pH = 7

a few drops of concentrated hydrochloric acid, and add 3 ml. in excess. Dilute to 250 ml., and heat to boiling. Set aside about 50 ml. of the solution, and while stirring run the standard ferrocyanide solution slowly from a buret into the main volume. A complex zinc ferrocyanide,

$$K_2Zn_3[Fe(CN)_6]_2$$

will be precipitated. While this should be white, a trace of iron not sufficient to interfere will usually render it bluish until near the end point, when the precipitate becomes white. This change in color is a guide but is not a reliable indicator. It is so useful that if the highest accuracy is not essential sometimes a drop of very dilute ferric chloride solution is introduced to provide this impurity.

Use a 5 per cent solution of uranyl nitrate or uranyl acetate, slightly acidified with acetic acid, on a spot plate as indicator. The end point is shown by a brown tinge appearing within 1 minute. When the end point is approximately located, add the balance of the solution and again heat to boiling. The end point can now be approached accurately and with reasonable promptness. A false end point can be obtained by titrating too rapidly. It is convenient to calculate the standardization in terms of zinc, zinc oxide, and zinc sulfide. If it is protected, this solution is stable for months.

CALCULATION OF STANDARDIZATION.

$$\frac{\text{Weight of zinc or zinc oxide}}{\text{Volume of ferrocyanide in ml.}} \times \frac{\text{equivalent weight of zinc compound desired}}{\text{equivalent weight of zinc or zinc oxide used}} = \text{factor for ferrocyanide per ml.}$$

PROCEDURE. Weigh out 0.2 to 0.3 gram of sample, dissolve in 30 ml. of 1:1 hydrochloric acid, and cool. If manganese, iron, or copper is present, it must be removed as follows: Add 35 ml. of a solution containing 50 ml. of concentrated ammonium hydroxide, 20 grams of ammonium chloride, and 75 ml. of water. This precipitates ferric and manganous hydroxides. Boil very gently for 1 to 2 minutes, and add excess of bromine water. This oxidizes the manganous to manganic hydroxide. Filter and wash thoroughly with a solution containing 10 per cent of ammonium chloride and 5 per cent of concentrated ammonium hydroxide. The precipitate can be reserved for later determination of the iron titrimetrically (page 194), or colorimetrically (page 195), and the manganese colorimetrically (page 198). Neutralize the filtrate with concentrated hydrochloric acid, and add 3 ml. in excess. Dilute to about 200 ml. with hot water, and heat nearly to boiling. Add 50 ml. of water saturated with hydrogen sulfide to precipitate small amounts of copper, or pass in hydrogen sulfide gas to precipitate large amounts. If small amounts were precipitated with hydrogen sulfide solution, use without removal of copper sulfide although its presence obscures the end point somewhat. If large amounts of copper are present so that hydrogen sulfide was passed in, filter and wash. The copper sulfide may then be saved for determination by conventional methods such as electrodeposition (page 323). If hydrogen sulfide gas was used, heat to boiling to remove most of the excess, for a large amount interferes. This separation of iron, manganese, and copper is unnecessary in a commercial zinc oxide pigment unless toners have been added. It is introduced here to clarify methods described later and to provide for analysis of paint pigments that have been toned with traces of mineral color.

Make the solution of sample, from which interfering substances have been removed if necessary, just alkaline with 1:1 ammonium hydroxide and then just acid with concentrated hydrochloric acid, adding 3 ml. in excess. Proceed as described for standardization (page 505), starting at "Dilute to 250 ml., and heat to boiling." Calculate as zinc oxide.

If the zinc oxide did not require separation of iron, manganese, or copper, for very accurate work a blank is automatically taken care of by standardizing the ferrocyanide at the same time. If other reagents had to be added in purification, for the highest accuracy a blank must be run on them, but not on the reagents used in standardization, and subtracted from the results obtained. This precaution is rarely required.

Calculation.

$$\text{Ferrocyanide solution in ml.} \times \text{factor for zinc oxide} \times \frac{100}{\text{weight of sample}} = \text{per cent zinc oxide}$$

If the pigment is straight zinc oxide, this should approximate 100 per cent.

Lithopone. Lithopone is a white pigment consisting of barium sulfate and zinc sulfide obtained by reacting zinc sulfate with barium sulfide and subsequent calcination. Therefore, the proportions are roughly chemically equivalent, 70 per cent barium sulfate and 30 per cent zinc sulfide. Sometimes zinc oxide or titanium oxide is also present.

Barium Sulfate or Insoluble Matter. To 1 gram of pigment in a 250-ml. beaker add 10 ml. of concentrated hydrochloric acid and then, in small quantities, about 1 gram of potassium chlorate. This oxidizes the sulfide. Evaporate to about half volume on a steam bath; then dilute with 100 ml. of water. Add 5 ml. of 1:10 sulfuric acid, and boil until the precipitate settles readily. Let stand a few minutes to settle, filter, wash, ignite, cool, and weigh. Save the filtrate for determination of zinc.

Qualitative examination of the original sample should have established whether titanium oxide is present and may have shown whether silica and alumina are present. If not, part of the precipitate can be tested for silica with hydrofluoric acid. In this treatment always add a few drops of sulfuric acid. Similarly test for alumina by fusion of a part with potassium acid sulfate. Dissolve this in water, filter, and add a small excess of ammonium hydroxide. If free from silica, titanium, and alumina, the insoluble matter is entirely barium sulfate.

Phase relationship $NH_4Cl - ZnO - H_2O$ (cont.)

The first runs on different concentrations of NH_4Cl in H_2O were carried out.

Standard Solution of Potassium Ferrocyanide.

$\frac{0.2 \text{ grams}}{32 \text{ ml}} = .00625 \text{ grs/ml}$.

Concentration $NH_4Cl - H_2O$ 10 grams NH_4Cl / 100 ml H_2O

Temperature	20 °C	0.4 grams of ZnO dissolved / 100 cc of NH_4Cl - Water.
"	40 °C	0.7 grams ZnO.
"	60 °C	1.3 gram ZnO.
"	80 °C	1.8 grams ZnO.

Concentration of $NH_4Cl - H_2O$ 15 grams / 100 cc

Temperature	20 °C	0.8 grams	ZnO	diss.	in	100 cc
"	40 °C	1.6	"	"	"	"
"	60 °C	2.6	"	"	"	"
"	80 °C	3.5	"	"	"	"

Luis Garcia Arcay

W. H. Burrows
3/13/69

March 14, 1969

Concentration NH_4Cl-H_2O: 20 grams /100 cc

Temperature	20°C	0.8 grams	ZnO	/100 cc	H_2O
"	40°C	1.6	"	"	"
"	60°C	4.6	"	"	"
"	80°C	7.5	"	"	"

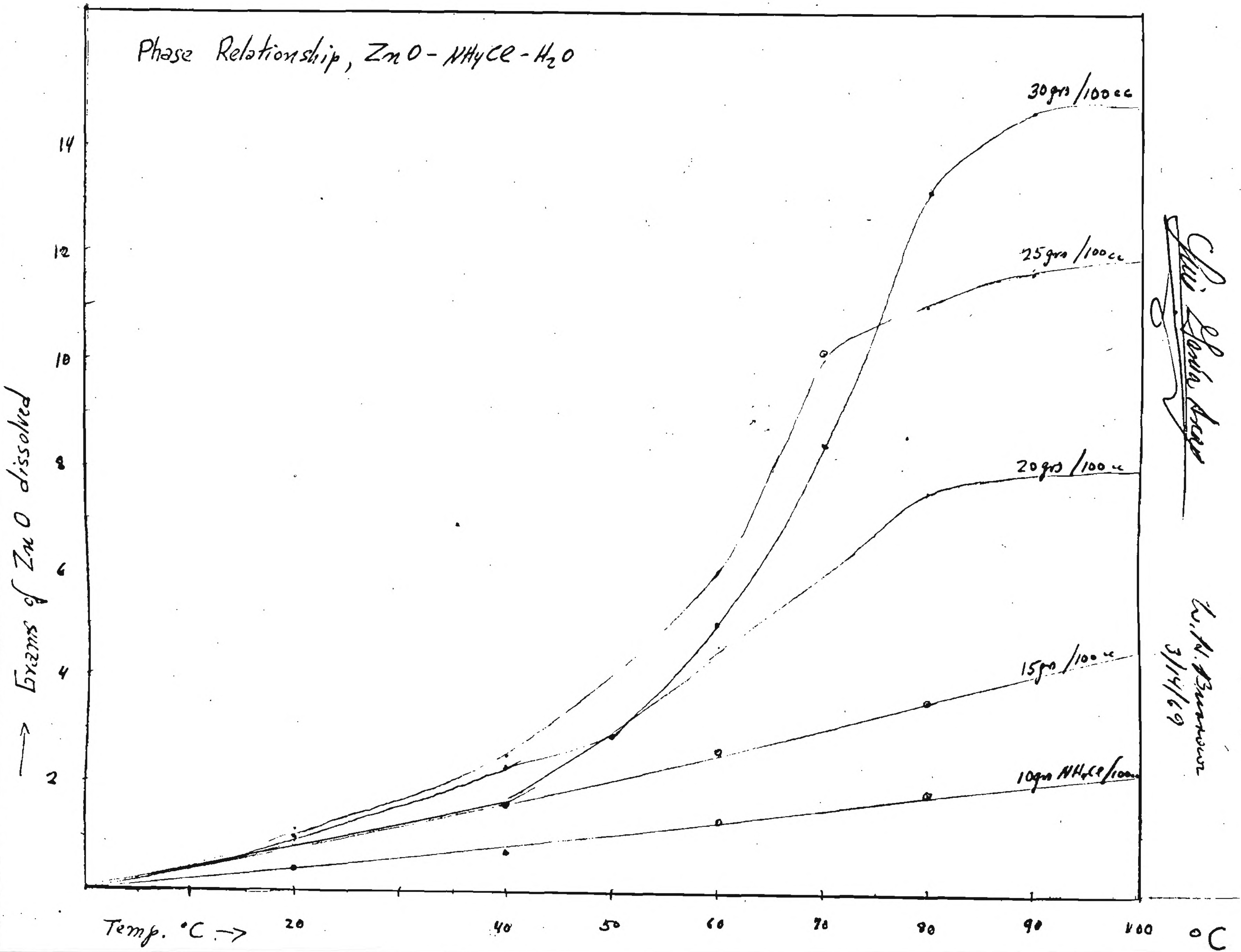
Concentration NH_4Cl-H_2O: 25 grams /100cc

Temperature	20°C	1.2 grams	ZnO	/100 cc	H_2O
"	40°C	2.5	"	"	"
"	60°C	6.0	"	"	"
"	70°C	10.2	"	"	"
"	80°C	11.0	"	"	"
"	90°C	11.6	"	"	"

Concentration NH_4Cl-H_2O: 30 grams /100cc H_2O

Temperature	20°C	1.0 gram	ZnO	/100 cc H_2O
"	40°C	2.3	"	"
"	50°C	3.4	"	"
"	60°C	5.0	"	"
"	70°C	8.4	"	"
"	80°C	13.2	"	"
"	90°C	14.6	"	"

Phase Relationship ZnO - NH4Cl-H


Phase Relationship, ZnO - NH4Cl - H2O
→ Grams of ZnO dissolved
2
4
6
8
10
12
14
Temp. °C →
20
40
50
60
70
80
90
100
°C
30 grs /100 cc
25 grs /100 cc
20 grs /100 cc
15 grs /100 cc
10 grs NH4Cl /100 cc

3/14/69

March 17, 1969

Phase relationship $NH_4Cl - NH_4OH - ZnO - H_2O$

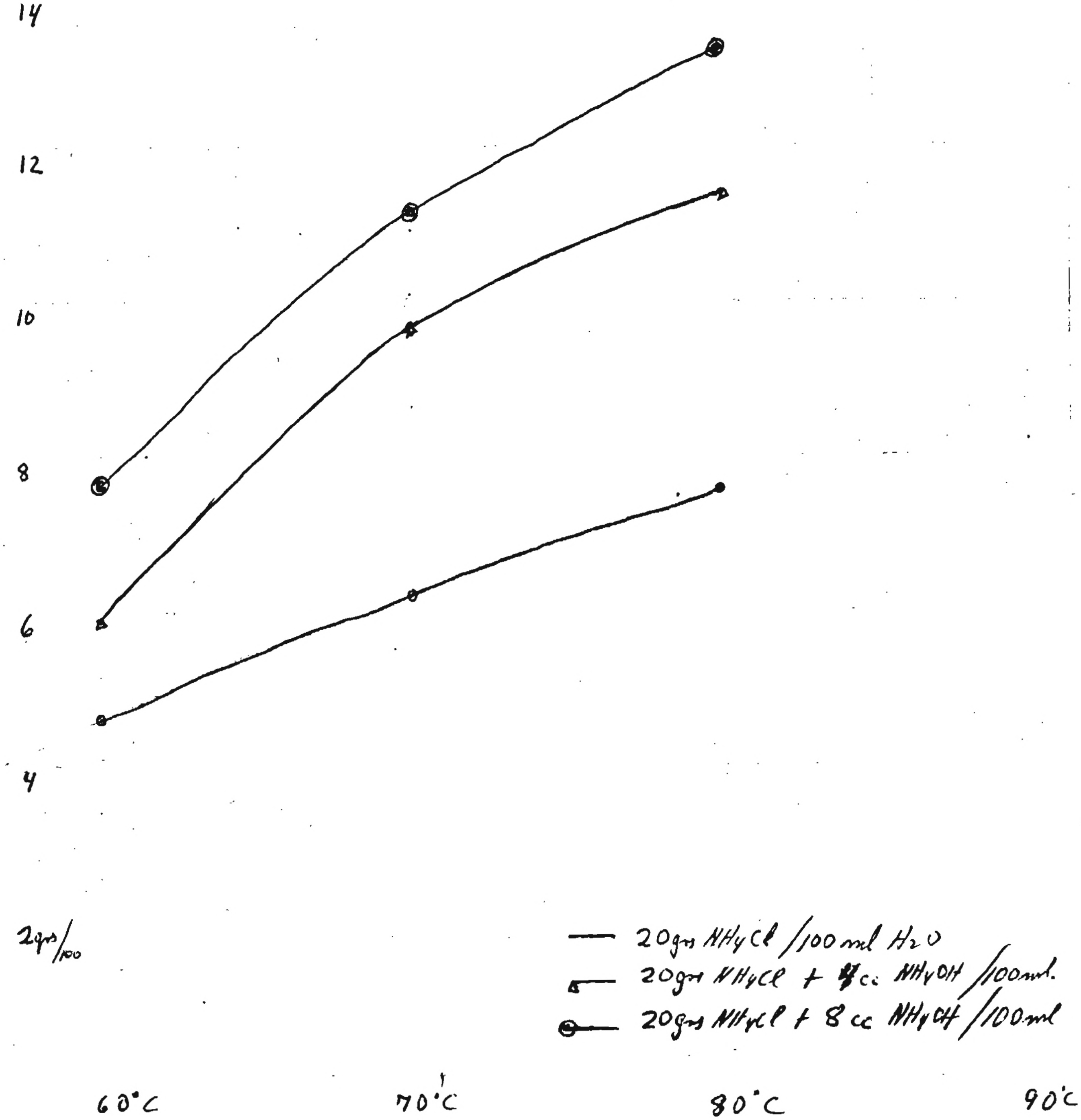
To the different concentrations of $NH_4Cl - H_2O$, small volumes of NH_4OH N.F grade were added and determinations of the ZnO dissolved were run.

Concentration: NH_4Cl 20grs/100cc H_2O + 4cc NH_4OH

Temperature	60°C	5.8 grams	of ZnO	diss.	/100cc
"	70°C	9.7	"	"	"
"	80°C	11.4	"	"	"

Concentration : NH_4Cl 20grs /100cc H_2O + 8cc NH_4OH

Temperature :	60°C	7.6 grs	ZnO	diss.	/100cc
	70°C	11.2	"	"	"
	80°C	13.3	"	"	"



[redacted]

[redacted]

MARCH 18, 1969

$NH_4Cl - ZnO - H_2O - NH_4OH$

Concentration: NH_4Cl - 25 grs/100cc H_2O + 4cc NH_4OH

Temperature	60°C	6.7 grs ZnO dissolved /100cc
"	70°C	11.9 grs " " "
"	80°C	13.3 grs " " "

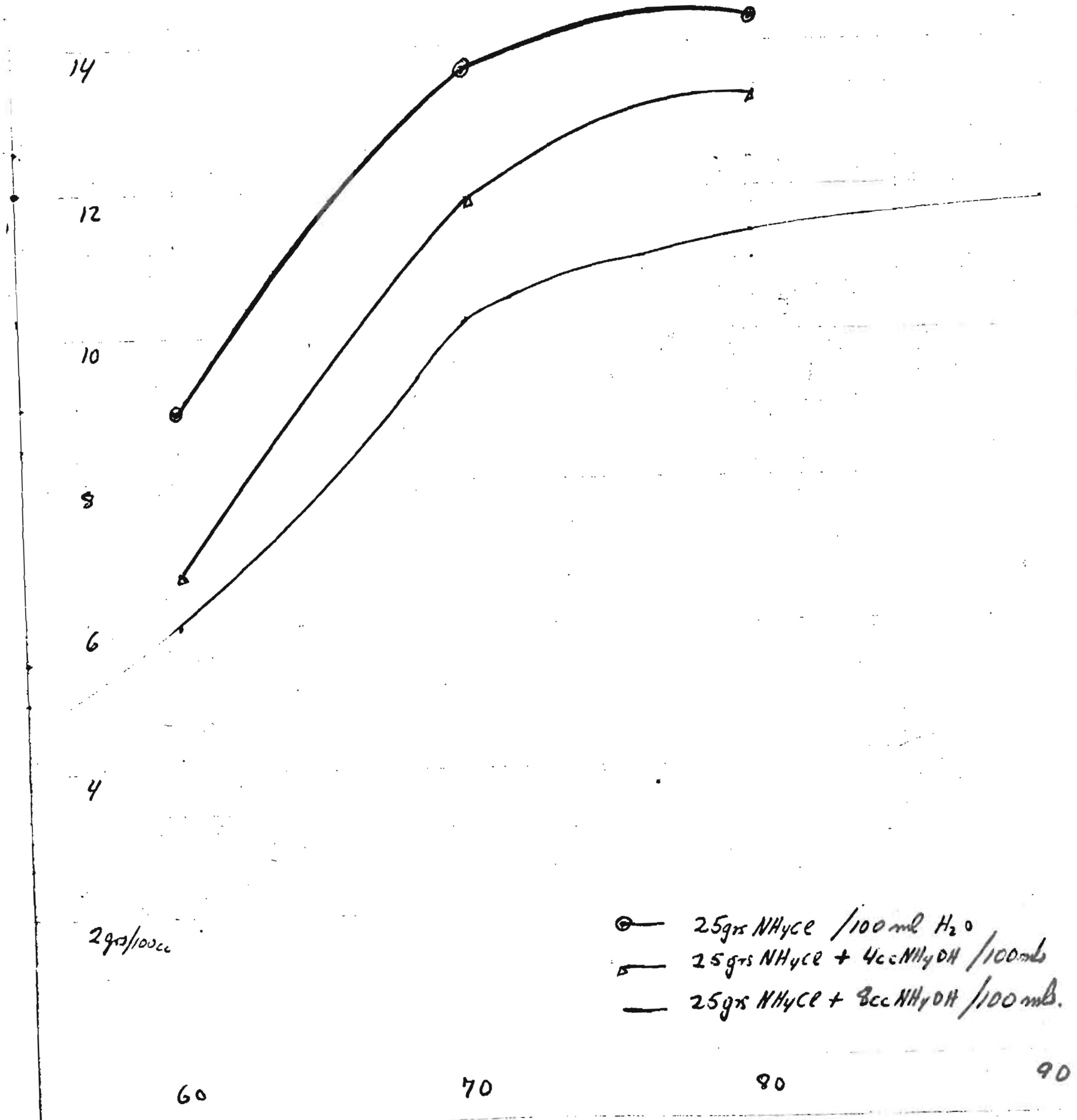
Concentration NH_4Cl 25 grs /100 cc + 8cc NH_4OH

Temperature	60°C	9.0 grs ZnO diss. /100cc
	70°C	13.7 grs " " "
	80°C	14.4 grs " " "

Concentration NH_4Cl 30 grs /100cc + 4cc NH_4OH

Temperature	60°C	6.2 grs ZnO diss. /100cc
	70°C	9.3 grs " " "
	80°C	16.2 grs " " "

14
12
10
8
6
4
2grs/1



[redacted]

[redacted]

March 19, 1969

Concentration: NH_4Cl 30grs/100cc + 8cc NH_4OH

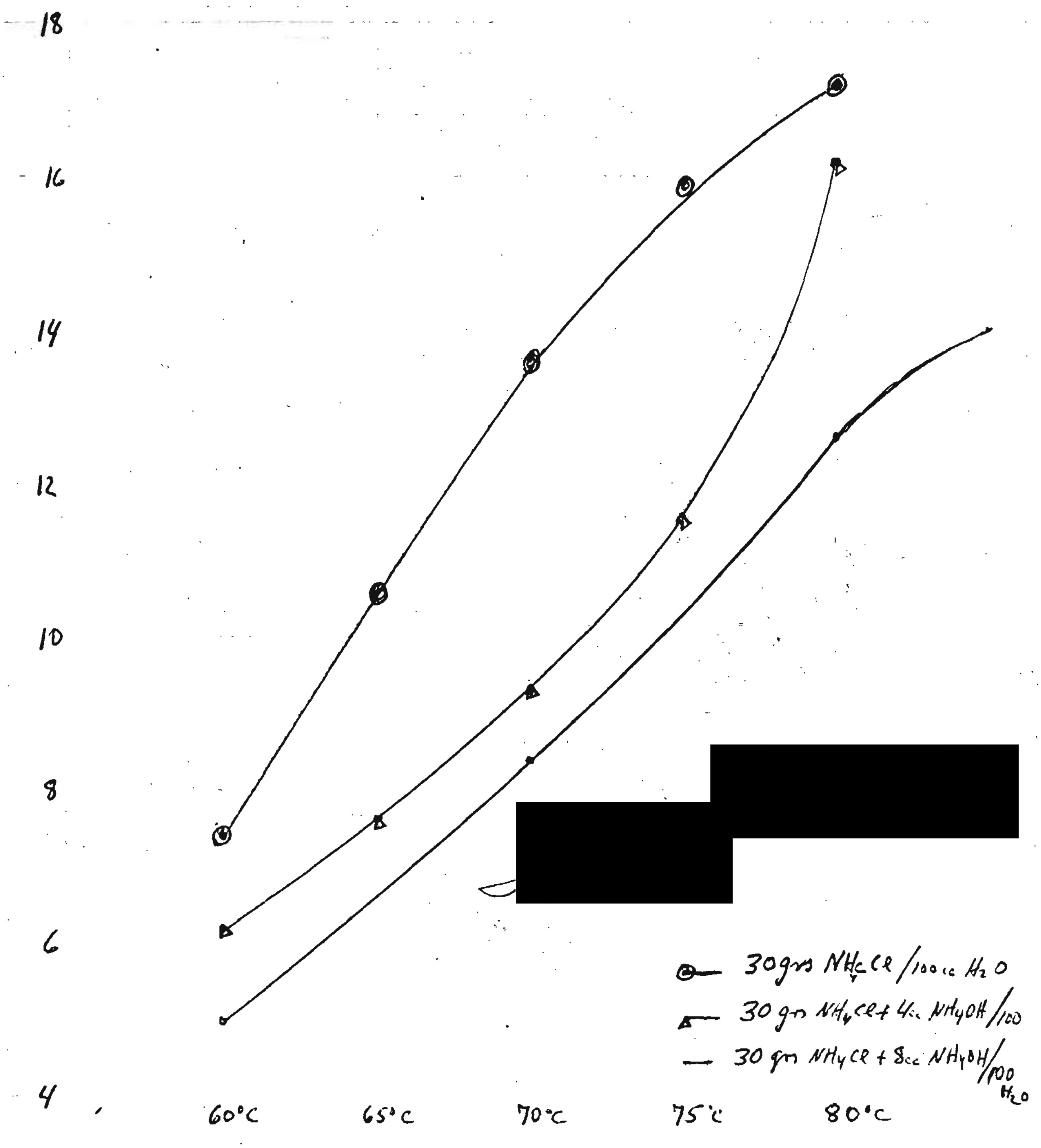
Temperature 60°C 7.4 grams ZnO diss/100cc
70°C 13.6 " " "
80°C 17.5 " " "

Above values run twice.

Temperature 65°C 10.5 grams " "

75°C 15.9 " " "

[redacted]


18
16
14
12
10
8
6
4
60°C
65°C
70°C
75°C
80°C
⊙ 30 grs NH4Cl /100 cc H2O
△ 30 gm NH4Cl + 4cc NH4OH/100
— 30 gm NH4Cl + 8cc NH4OH/100 H2O

[redacted]

March 20, 1969

Extraction of ZnO from Fly Ash.-

100 grams of Fly Ash containing approximately 40 grs of ZnO were extracted with NH_4Cl solvent (30grs/100cc H_2O). for 30 min. at a temp of 80-90°C.

After extraction, it was allowed to settle in an oven (80-90°C) for 2-3 hours.

The liquid was decanted and the whole filtered until dry.

This solvent was let cool and crystallize overnight.

Amount of Solvent used	300cc
" " " recovered	140 cc

Aprox. pH before extraction	6.5
" " after "	6.5

[redacted] [redacted]

Marc

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wt.

%

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Th

March 21, 1969

The Zn O was recovered from the solvent by vacuum filtration and washed about 5 times with cold water followed by hot water.

wt. of dried Zn O 25 grams.
% of solvent recovered 46.7%

A second extraction was started
Amount of Solvent used and procedure of extraction was the same as the first.

The extraction was left to crystallize overnight.

[redacted]

March 24, 1969

The crystallized ZnO was recovered from the solvent and washed with cold water followed by hot water until reasonably free of Chlorides.

Approx. PH of the solvent: 6.5
% of solvent recovered 48%

Wt. of ZnO recovered (dried) 26 grams

0.5 grams of Fly Ash were extracted in HCl and further extractions were carried out in order to get rid of the lead, copper, Iron, etc.
ZnO determination by the K Ferrocyanide test was 86%.
This high value was probably due to the incomplete precipitation of Fe.

[redacted]

[redacted]

March 25, 1968

0.3 grams of ~~Fly~~ Ash were extracted and analyzed for ZnO.

Amt. ZnO = 0.138 grams = 46%

2nd Extraction 0.138 grams = 46%

3rd Extraction 0.137 grs = 45.7%

4th Extraction 0.143 grs = 47%

[redacted]

[redacted]

March 26, 1969

One Pound of Fly Ash was extracted using NH_4Cl solvent with a concentration of 30 grams/100cc
408 grams of NH_4Cl were dissolved up to 1362cc
The solvent was heated to 85° - 90° and the Fly Ash was added.
After extracting for ½ hour the Solution was put into an oven and let settle for about 2-3 hours.

lite

It was then decanted and filtered, using vacuum and infrared lamp to keep the Temperature up, and avoid crystallization. The recovered solvent was left to cool overnight.

10 grams of F. Ash were taken and extracted 3 times with concentrated NH_4OH (50 mls. portions) The NH_4OH was evaporated to dryness and the precipitate dissolved in dilute HCl.
A ZnO determination was run giving only .57 grams ZnO extracted.

[redacted] [redacted]

Removal Of The Corrosion Test Spool From Test

At the termination of the test exposure, the corrosion test spool should be immediately and thoroughly washed with water to remove all of the corrosive. This should be done in such a manner as to minimize damage to corrosion products on the surface of the specimens, but it should also be assured that the corrosive does not remain beneath these products. In severe cases, neutralization of the corrosive may be desirable. Following washing, the test specimens should be allowed to dry completely. The spool should then be carefully packed to prevent damage to the specimens during shipment.

All exposed corrosion test spools should be returned to the following address:

THE INTERNATIONAL NICKEL COMPANY, INC.
HARBOR ISLAND CORROSION LABORATORY
POST OFFICE BOX 656
WRIGHTSVILLE BEACH, NORTH CAROLINA
ATTENTION: MR. E. A. BAKER

If the identification number on the spool assembly has been obliterated by corrosion, the spool should be tagged with this number to facilitate identification.

It is also advisable to write a covering letter to the Corrosion Engineer who arranged with you for the corrosion test spool, with a copy to the Harbor Island Corrosion Laboratory, indicating that the spool is being returned. This letter should indicate the request number of the spool.

Information On The Corrosion Environment

Corrosion tests are of significant value only when the conditions of the test exposure are accurately known. The major corrosion conditions that must be accurately known are (1) the corrosive (principal substances, impurities, composition, concentration, pH, etc.), (2) temperature, (3) aeration, (4) velocity conditions and (5) duration of the test exposure. Also, such information as the process involved, type of process unit, location of the spool in the unit and past experiences with materials of construction in the particular corrosion environment should be furnished. This information can be conveniently supplied on the "RECORD OF CORROSION TEST EXPOSURE" form supplied with these instructions. Three copies of this form are provided for each corrosion test spool exposure. These forms should be completed in triplicate, with one copy being retained in your file for record purposes, and the other two copies attached to your letter to the Corrosion Engineer and to the Harbor Island Corrosion Laboratory.

On receipt, the corrosion test spool will be disassembled and the individual test specimens cleaned and reweighed. Corrosion rates, based on the length of test exposure and the weight loss, will be determined. Each specimen will be carefully examined for evidence of pitting, crevice corrosion, cracking or other forms of localized attack. The depth of pitting or crevice corrosion will be measured.

Reporting Of Corrosion Test Results

The corrosion rates and other information developed from examination of the test specimens, and the test specimens, will be sent to the Corrosion Engineer who arranged with you for the corrosion test spool. These specimens will again be carefully examined and the corrosion test results carefully reviewed.

A full report of the results of the corrosion spool test exposure will be prepared, and will include all pertinent information furnished concerning the test exposure. This report will be sent to you along with a covering letter giving any additional comments that the Corrosion Engineer may wish to make concerning the test results, suggested materials of construction and other pertinent comments that may be helpful to you in selecting a material of construction. If you have withheld information concerning the corrosion environment or the nature of the process, please advise the Corrosion Engineer so that this may be kept in mind in analyzing the test results.

R. A. Covert
May 1, 1968

Printed in U. S. A.

SF 7 4 2 1 0 TENS THOUSANDS | SF 7 4 2 1 0 THOUSANDS | SF 7 4 2 1 0 HUNDREDS | SF 7 4 2 1 0 TENS | SF 7 4 2 1 0 UNITS

COMPANY

FILE No. I/33-84/41
SPOOL No. 2
DATE 1/7/42
wzf/cws

ORROSIVE MEDIA & CONC: 28 to 40% Ammonium Chloride

S.R. 5677

COMPANY

NDUSTRY: Chemical
7 - Metal Works (Galvanizing)

ROCESS INVOLVED: Production of galvanizer's ammonium chloride

ROCESS UNIT: Evaporating tank

OCATION OF SPECIMENS: Immersed

YPE OF TEST: Spool

DURATION OF TEST: 762 hrs (32 days)

EMPERATURE: 25 - 102°C. (77 - 216°F.)

AERATION:

AGITATION:

ENERAL REMARKS:

28% liquor at 25°C. was charged to tank and evaporated to 40% liquor at 102°C. In between batches, spool was not exposed. Actual period of exposure -- 762 hrs (32 days)

METAL	SPEC. CODE	CORROSION RATE			PITTING DURING TEST–IN.		
		MDD.		IN./YR.	SURFACE		MAX. UNDER SPACER
		EACH	AV.	AV.	MAX.	AV.	
Monel	Mee	75.8					
	Med	69.7	72.7	0.012			
Nickel	Nfz	57.6					
	Nfy	46.4	52.0	0.0084			
Inconel	NCbh	2.9			0.006	0.005	0.006
	NCbg	3.1	3.0	0.0005	0.005	0.004	0.005
Copper	Ckw	726.0					
	Ckx	674.0	700.0	0.113			
18-8-3 Mo Stainless	RMab	3.3			0.010	0.008	0.008
	RMai	1.7	2.5	0.0005	0.006	0.006	0.008
Hastelloy C	HCcg	0.013					
	HCcf	0.29	0.15	0.00002			
Ni-Resist	JAvm	62.5					
	JAwl	63.3	62.9	0.012			
Cast Iron	Jaht	1580.0					
	Jahu	1980.0	1780.0	0.356			

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION

225 North Avenue, Northwest · Atlanta, Georgia 30332

May 8, 1969

Kerr-McGee Chemical Corporation
Kerr-McGee Building
Oklahoma City, Oklahoma 73102

Attention: Mr. L. E. Craig
Vice President - Manufacturing

Subject: Monthly Report No. 2, Project A-1153
Zinc Oxide Recovery Process
Covering the period April 1, 1969 through April 30, 1969

Gentlemen:

Enclosed are copies of our laboratory notes for the subject period. Because of activities incident upon procurement and receipt of materials for the pilot plant operation, together with related activities, it has not been possible to devote much time to laboratory work. The following observations may, however, be made from the work done last month and this month.

Yields of both zinc oxide and recovered solvent have improved with experience in conducting the extraction. However, it will still remain for the pilot plant to demonstrate the maximum that can be achieved in this direction.

Some solvent is apparently occluded in the crystallized zinc oxide. This is not readily removed by simply washing the crystals; however, a combination of washing and grinding procedures reduces the solvent content to a satisfactorily low level. For some applications, residual ammonium chloride in the zinc oxide would probably not be detrimental.

With respect to the corrosion testing with International Nickel Co., Mr. Oxford has provided us with a copy of IN's Corrosion Engineering Bulletin CEB-3. Page 28 of this bulletin, Table 32 gives results obtained with test spools immersed in ammonium chloride solutions (during evaporation from 28 to 40 per cent NH_4Cl) at 216° F. Duration of the test was 762 hours, which is probably more time than we could accumulate, without a special set-up, during the pilot plant operation. With these results available, we are inclined toward omitting the proposed spool tests.

Much progress has been made in setting up the pilot plant; however, because of inadequate facilities in the C.E. Annex, we have had to move to the fourth floor of the Chemical Engineering Building, the site originally planned for this operation. This has occasioned only slight delay, and we should be in operation within the next two weeks.

Respectfully submitted,

[redacted]

W. H. Burrows
Project Director

WHB:sm
1 Enclosure

March 31, 1969

One pound of F. Ash was extracted with solvent already used in a previous extraction.
The procedure was the same as in the other extractions.

It was left overnight to crystallize.

Luis Garcia Arcau.

3/31/69

April 1, 1969

Amount of ZnO extracted = 105 grams = 23%
" " Solvent recovered = 1,126 cc = 83%

20 grams of F. Ash were extracted with 250 cc of previously used solvent (approx. 20 gr/100 concentr.) at a temperature of 60°C

The filtrate was cooled overnight at 10°C

[redacted] [redacted]

April 2, 1969

The ZnO recovered was washed with 800cc cold water followed by 2 liters of hot water
The ZnO was dried with an infrared lamp for 2 hours and then weighted.

wt of the F. Ash = 20 grams
wt. " ZnO = 6.48 grams
% of ZnO recovered = 32.4%
ZnO remaining in Solvent = 1.5 grams.
% " " " " = 7.5%

Total ZnO in F. Ash 42%

[redacted]

[redacted]

April 3, 1969

One lb. of F. Ash was extracted following the same procedure as with previous extractions. The amount of solvent used was 1500cc at a concentration of 30gm NH_4Cl/100cc H_2O. After Filtration, The extracted ZnO was left to crystallize overnight.

Two .3gram samples of F. Ash were extracted in HCl and after elimination of Pb, Fe, Cu, etc. a ZnO determination was run using the standard K Ferrocyanide Test.

Results:

a) .126 grams = 42% ZnO

b) .129 " = 43% "

[redacted] [redacted]

April 4, 1969

The crystallized ZnO was washed with cold water followed by hot water until fairly free of Cl^-

Volume of Solvent recovered 1200cc = 80%
ZnO extracted 126 grams = 27.7%

[redacted]

April 7, 1969

[redacted]

April 7, 1969

Further purification of ZnO.

Samples of ZnO, extracted by previous methods, were washed in hot water first then cold water until the Cl^- concentration seemed low*. Some samples at this step were saved for controls, the rest were put into a ball mill overnight.

* Visual test using $AgNO_3$ reagent

[redacted]

April 8, 1969

Further Purification of ZnO (cont.)

The ZnO in the form of a slurry was taken out of the ball mill and filtered.

The filtrate was saved and chloride determinations were run.

A specific ion electrode for Chloride was used for this determination after calibration against standard Chloride solution.

[redacted]

April 10, 1969

Purification of ZnO (cont.)

Samples of the already ~~[illegible]~~ ground ZnO were washed again in hot and cold water and then dried in an oven at 105°C for 4 hours.

Other samples were left in the oven over-night.

[redacted]

April 11, 1969

Purification of ZnO (cont.)

The dried ZnO was dissolved in 1:2 HNO_3 and chloride determinations were run in several samples.

Results:

1) Washed ZnO (Filtrate) = 2% Cl^- concentration.
2) Ground and washed ZnO = .2% Cl^- "

[redacted]

April 15, 1969

Purification of ZnO.

A new set of samples from Fly Ash extractions were taken, and the procedure for the elimination of NH_4Cl was the same as the one used in the preceding two pages.
Samples were left overnight in the ball mill.

[redacted] [redacted]

April 16, 1969

The slurry was filtered and the filtrate saved for Cl^- determination.

Chloride Concentration of filtrates = 2 %
The ZnO was saved for further washings.

[redacted] [redacted]

April 17, 1969

The already ground ZnO was washed with hot and cold water and then dried overnight at 105°C

[redacted] [redacted]

April 22, 1969

Purification of ZnO (cont.)

Samples of dried ZnO were taken and dissolved in 50 cc 1:2 HNO_3 and chloride determinations were run.

Results:

ZnO (Filtrate) after ball mill ground 2%
ZnO after ground and repeated
water washings .2%

[redacted]

[redacted]

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION

225 North Avenue, Northwest · Atlanta, Georgia 30332

June 9, 1969

Kerr-McGee Chemical Corporation
Kerr-McGee Building
Oklahoma City, Oklahoma 73102

Attention: Mr. L. E. Craig
Vice President - Manufacturing

Subject: Monthly Report No. 3, Project A-1153
Zinc Oxide Recovery Process
Covering the period May 1, 1969 through May 31, 1969

Gentlemen:

Laboratory activities on this project have been suspended, pending start-up of the pilot plant operation. Consequently, there are no notebook entries for this month.

Samples of zinc oxide product have been submitted to the microscopy laboratory, and a sample of fly ash to the spectroscopy laboratory. However, because of illness of key personnel in those laboratories, there is no report at present on their findings.

We expect to make our first runs in the pilot plant during the week of June 9 to 13.

Respectfully submitted,

[redacted]

W. H. Burrows
Project Director

WHB:sm

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

July 8, 1969

Kerr-McGee Chemical Corporation
Kerr-McGee Building
Oklahoma City, Oklahoma 73102

Attention: Mr. L. E. Craig
Vice President - Manufacturing

Subject: Monthly Report No. 4, Project A-1153
Zinc Oxide Recovery Process
Covering the period June 1, 1969 through June 30, 1969

Gentlemen:

Activities during the current month have been confined to initial runs in the pilot plant. Copies of the pilot plant notebook entries for this period are attached.

Inasmuch as installation procedures were still under way during most of this time, including additional provisions for exhausting ammonia fumes, modifications of the processor and filter, adjustments of the pre-heaters, etc., it has not been possible to make a large number of runs.

Those runs that have been made have confirmed the method previously developed in the laboratory, including the extraction of zinc oxide, and the separation of lead and copper. One departure from laboratory results has, however, proved a source of annoyance. In the laboratory preparation, the hot solvent passed the filter with only its burden of zinc oxide; the iron oxide was all successfully retained. In the pilot plant, a small amount (analyses are under way) of colloidal ferrous hydroxide is carried through the filter. In the crystallization bath, this compound is oxidized to ferric oxide, which precipitates with the zinc oxide, causing discoloration of the latter. Studies are presently being conducted to determine the most expeditious method of removing this feature of the process.

As soon as this has been done, we shall proceed with the materials balance studies and other features of the research project.

Respectfully submitted,

[redacted]

W. H. Burrows
Project Director

WHB:sm
1 Enclosure

LABORATORY NOTEBOOK
No. 2

JUNE 11, 1969, THROUGH

Project No. A-1153
Pilot Plant Phase
for
KERR-McGEE CHEMICAL CORP.

by
W. H. Burrows
Project Director

This notebook will be devoted to the development of and optimization of the process variables of the proposed process for extracting zinc oxide from ~~[illegible]~~ steel furnace flue dust on a pilot plant scale. Some of the variables studied will be: ptimum amount of Zn dust added to the solvation reaction in order to displace all copper and lead, optimum crystallization conditions for the desired crystal size, amount of solvent losses and optimum conditions for minimizing solvent loss, possibility of recovering both lead and copper from fly ash by postponing the addition of Zn dust until after filtration.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-16-69 Batch No. 616-1

Solvent Temperature During Solvation: Initial: 60 °C Final: 101.7 °C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 1.0 Fly Ash Batch No. 1

Solvation Started at: 1120 Finished at: 1237

Agitator Setting Max. RPM

Settling Started at: 1237 ; Temperature 99 °C.

Settling Finished at: 1500 ; Temperature 85 °C.

Mother Liquor Pumped to Crystallizer at 1500

Crystallizer Temperature after Pumping was 66.5 °C.

Comments:

Settler Temp., °C	Time
99.0	1237
89.0	1337
86.5	1437
85.0	1500

AM of June 17 after crystallization: Reddish-brown material crystallized with ZnO crystals. ZnO crystals were relatively large and of monoclinic form. After numerous washings, first with cold tap water, then with hot tap water, ZnO crystals were still of off-white color. Supernatant NH_4Cl solvent was light green in color.

ZnO Recovery Pilot Plant Log Sheet

Date: 6-17-69 Batch No. 617-1

Solvent Temperature During Solvation: Initial: 61.5°C Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 1

Solvation Started at: 1415 Finished at: 1530

Agitator Setting Max RPM

Settling Started at: 1530 ; Temperature 99°C.

Settling Finished at: 1610 ; Temperature 96.7°C

Mother Liquor Pumped to Crystallizer at 1610

Crystallizer Temperature after Pumping was 68°C.

Comments:

Settler Temp, °C.	Time
99.0	1530
97.2	1540
97.0	1545
96.8	1600
96.7	1610

Approximately ½ gal. of fly ash slurry was inadvertantly pumped to the crystallizer.

AM of June 18 after crystallization: Reddish-brown material crystallized along with ZnO crystals. Supernatant solvent was light green in color

ild steel tee replaced
racked pvc tee on discharge
de of gear pump for this
atch only

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-18-69 Batch No. 618-1

Solvent Temperature During Solvation: Initial: 60°C. Final: 101.7°C.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 1

Solvation Started at: 1045 Finished at: 1200

Agitator Setting Max. RPM

Settling Started at: 1200; Temperature 98.0°C.

Settling Finished at: 1415; Temperature 94.0°C

Mother Liquor Pumped to Crystallizer at 1415

Crystallizer Temperature after Pumping was —

Comments:

Settler Temp, °C	Time
98.0	1200
96.2	1205
96.2	1225
96.0	1235
96.0	1245
95.5	1315
94.0	1415

Nickel coated agitator shaft and props were replaced with monel unit just prior to this run. Mild steel tee on gear pump discharge side was replaced with pvc tee prior to this run.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-18-69 Batch No. 618-2

Solvent Temperature During Solvation: Initial: 64°C Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0,948 Fly Ash Batch No. 1

Solvation Started at: 1315 Finished at: 1430

Agitator Setting Max RPM

Settling Started at: 1430 ; Temperature 95.0°C

Settling Finished at: 1615 ; Temperature —

Mother Liquor Pumped to Crystallizer at 1615

Crystallizer Temperature after Pumping was —

Comments:

AM of 6-19-69 (830):

Crystals from mother liquor of batches 618-1 + 618-2 were large, monoclinic, + white. A small amount of dark residue had ppt. with the crystals. Supernatant solvent was green. The top filter disk and its retained brown material was submitted for chemical analysis after pumping the "dirty" solvent from batches 618-1 and 618-2 from the crystallizer

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: June 18, 1969 Batch No. 618 - 3

Solvent Temperature During Solvation: Initial: 68 °C Final: 101.7°C.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 1

Solvation Started at: 1455 Finished at: 1600

Agitator Setting Max RPM

Settling Started at: 1600 ; Temperature —

Settling Finished at: 1200 June 19 ; Temperature 81.5°C.

Mother Liquor Pumped to Crystallizer at 1200 June 19

Crystallizer Temperature after Pumping was 61°C

Comments:

Slurry was allowed to settle overnite in retention drums. Temp. in retention drums at 845 on 6-19 was 83°C. Crystallization started at ~ 1430. Crystallizer temperature at this time was ~42°C. Crystals were smaller than encountered previously but were still dirtied by brown solid material.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-19-69 Batch No. 619-1

Solvent Temperature During Solvation: Initial: 60°C Final: 101.7°C

Reactor Charge: Gallons Solvent 60 (fresh) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 2

Solvation Started at: 1300 Finished at: 1412

Agitator Setting Max. RPM

Settling Started at: 1412 ; Temperature 97.8°C

Settling Finished at: ~1400 ~~July~~ June 20 ; Temperature —

Mother Liquor Pumped to Crystallizer at ~1400 ~~July~~ June 20

Crystallizer Temperature after Pumping was —

Comments:

a fresh batch of 60 gallons of 30% NH_4Cl solvent was made in the reactor after meticulous cleaning in order to determine whether the brown material ppt. with the crystals would precipitate using fresh solvent. A sample of 619-1 and 619-2 supernatant liquor which had been filtered with the plant filter were allowed to crystallize in separate flasks. The crystals from both batches contained entrained brown material and the supernatant liquor from both batches was brownish green.

A sample of the slurry from this batch was taken by L. Garcia and heated, filtered, and crystallized in the lab. Water-white filtrate and pure white crystals resulted.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-19-69 Batch No. 619-2

Solvent Temperature During Solvation: Initial: 65°C Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 2

Solvation Started at: 1420 Finished at: 1525

Agitator Setting Max RPM

Settling Started at: 1525; Temperature 92°C

Settling Finished at: ~1400 June 20; Temperature —

Mother Liquor Pumped to Crystallizer at ~1400 June 20

Crystallizer Temperature after Pumping was —

Comments:

AM of June 23: Crystals from batches 619-1 + 2 were off white due to entrained brown material. Crystals were large and monoclinic.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-24-69 Batch No. 624-1

Solvent Temperature During Solvation: Initial: 64°C Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 2

Solvation Started at: 1135 Finished at: 1245

Agitator Setting Max RPM

Settling Started at: 1245 ; Temperature 91°C

Settling Finished at: 1000 June 25 ; Temperature 77°C

Mother Liquor Pumped to Crystallizer at 1000 June 25

Crystallizer Temperature after Pumping was 64°C.

Comments:

Batches 624-1 & 2 were pumped from the retention drums through a 12 disc arrangement (instead of 10 filter discs) with the Alsop filter. The filtrates of both batches, pumped together into the crystallizer appeared clear but slightly brown in color initially. After a few minutes residence time in the crystallizer, the solution turned to a deep brown and immediately thereafter precipitation of iron oxide was noticed.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-24-69 Batch No. 624-2

Solvent Temperature During Solvation: Initial: 62°C. Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 2

Solvation Started at: 1300 Finished at: 1415

Agitator Setting Max RPM

Settling Started at: 1415; Temperature 95°C

Settling Finished at: 1020 June 25; Temperature 82°C

Mother Liquor Pumped to Crystallizer at 1020 June 25

Crystallizer Temperature after Pumping was 64°C

Comments:

AM of June 26: Batches 624-1 & 2 have crystallized. A heavy scum of iron oxide was noted on the top of the crystallizer solvent.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-25-69 Batch No. 625-1

Solvent Temperature During Solvation: Initial: — Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 2

Solvation Started at: 1200 Finished at: 1315

Agitator Setting Max RPM

Settling Started at: 1315; Temperature —

Settling Finished at: 1345 June 26; Temperature 70°C

Mother Liquor Pumped to Crystallizer at 1345 June 26

Crystallizer Temperature after Pumping was 69°C

Comments:

The new Monel immersion heaters were installed just prior to this batch.

Batches 625-1 & 2 were filtered from the retention drums through 12 discs of "10 micron" polypropylene (filter medium PO 7032) to the crystallizer.

After filtration, the mother liquor in the crystallizer was unclear and very dark brown in color.

AM, June 26: After crystallization of batches 625-1 & 2, the crystals were contaminated with the brown iron oxide

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-25-69 Batch No. 625-2

Solvent Temperature During Solvation: Initial: — Final: 101.7°C.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 2

Solvation Started at: 1320 Finished at: 1445

Agitator Setting Max RPM

Settling Started at: 1445; Temperature —

Settling Finished at: 1340 June 26; Temperature 80°C.

Mother Liquor Pumped to Crystallizer at 1340 June 26

Crystallizer Temperature after Pumping was 77°C.

Comments:

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-26-69 Batch No. 626-1

Solvent Temperature During Solvation: Initial: — Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 3

Solvation Started at: 1315 Finished at: 1430

Agitator Setting Max RPM

Settling Started at: 1430; Temperature —

Settling Finished at: 1345 June 27; Temperature —

Mother Liquor Pumped to Crystallizer at 1345 June 27

Crystallizer Temperature after Pumping was —

Comments:

The supernatant liquid from the retention drums after settling batches 626-1 & 2 were pumped to the bath thru the Alsop filter using 12 of the 15 micron Cuno discs as media. The discs were precoated with ~ 50 gms. of the filter aid prior to filtration by pumping a filteraid-water slurry thru the filter. Mother liquor pumped into the crystallizer was relatively clear and had a light yellow-brown hue.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: 6-26-69 Batch No. 626-2

Solvent Temperature During Solvation: Initial: — Final: 101.7°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 3

Solvation Started at: 1440 Finished at: 1555

Agitator Setting Max RPM

Settling Started at: 1555; Temperature —

Settling Finished at: 1400 June 27; Temperature —

Mother Liquor Pumped to Crystallizer at 1400 June 27

Crystallizer Temperature after Pumping was —

Comments:

AM, June 30: Mother liquor from batches 626-1 & 2 was allowed to crystallize over the weekend. Large, monoclinic, very white crystals of ZnO were obtained. A relatively small amount of iron oxide had also precipitated to the bottom of the crystallizer but did not contaminate the ZnO.

[redacted]

[redacted]

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

August 5, 1969

Kerr-McGee Chemical Corporation
Kerr-McGee Building
Oklahoma City, Oklahoma 73102

Attention: Mr. L. E. Craig
Vice President - Manufacturing

Subject: Monthly Report No. 5, Project A-1153
Zinc Oxide Recovery Process
Covering the period July 1, 1969 through July 31, 1969

Gentlemen:

Copies of the pilot plant notebook for the subject period are attached.

As pointed out in our Monthly Report No. 4 dated July 8, and in our letter dated July 15, operation of the pilot plant has been hindered and delayed by complications involved in the installation of special precautionary features to handle ammonia fumes and by the presence of iron oxide in the filtrate during the crystallization process. As of the present writing, however, the tasks of the pilot plant phase have been completed within sight of the original goals. The source of iron oxide contamination has been traced and eliminated, the preferred process modification has been confirmed, and a materials balance has been run.

We outlined in a letter (July 30) to Dr. Craig the sources of iron oxide contamination, as follows:

(1) Since the preheaters were incapable of bringing the solvent up to working temperature, we were using the processor to bring it up from ca 150 to 215° F., a period of $1\frac{1}{2}$ to 2 hours, during which time the flue dust and solvent were in contact. This was a much larger digestion period than we had used in the laboratory.

(2) Zinc dust was being added during this digestion period. Apparently, nascent hydrogen, produced by reaction of the zinc and HCl (from hydrolysis of ammonium chloride) was reducing a portion of the Fe_3O_4 to $Fe(OH)_2$ which, in colloidal form, was passing the filter and causing the trouble.

As a consequence of these findings, the straight process was eliminated, and the materials balance was determined for Process Modification II, only. The product obtained by this process is of excellent appearance. Examination and analysis of this product is now being completed.

Upon completion of present laboratory studies, we shall be able to complete our materials balance details and prepare our Final Technical Report. Our anticipated date for this report is August 18.

Respectfully submitted,

[redacted]

W. H. Burrows
Project Director

WHB:sm
1 Enclosure

ZnO Recovery Pilot Plant Log Sheet

Date: July 1, 1969 Batch No. 71-1

Solvent Temperature During Solvation: Initial: — Final: 101.7°C.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 3

Solvation Started at: 1030 Finished at: 1220

Agitator Setting Max RPM

Settling Started at: 1220 ; Temperature —

Settling Finished at: 1100 July 2 ; Temperature —

Mother Liquor Pumped to Crystallizer at 1100 July 2

Crystallizer Temperature after Pumping was 52°C

Comments:

The supernatant liquor from batches 71-1 & 2 (in 3 separate barrels) was pumped and filtered to the crystallizer using the Alsop filter. Each barrel of supernatant liquid was filtered thru a new 12 disc set of 15 micron Cuno filters after precoating with 50 grams of Solka floc. A 1000 ml. sample of filtrate from the filter discharge hose was taken after each barrel was ~½ filtered. The supernatant liquid in each barrel was allowed to drop to a specific temperature before filtering.

Sample 1; 79°C in barrel; 76°C at filter discharge
Sample 2; 69°C in barrel; 66°C at filter discharge
Sample 3; 59°C in barrel; 57°C at filter discharge

The 3 samples were allowed to crystallize in the

[redacted] [redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 1, 1969 Batch No. 71-2

Solvent Temperature During Solvation: Initial: — Final: 101.7°C.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 3

Solvation Started at: 1310 Finished at: 1500

Agitator Setting Max RPM

Settling Started at: 1500; Temperature —

Settling Finished at: 1200 July 2; Temperature —

Mother Liquor Pumped to Crystallizer at 1200 July 2

Crystallizer Temperature after Pumping was 52°C.

Comments:

flasks overnite. All 3 samples were clear but brownish-yellow initially. It was noted that crystallization began at 43.2°C. in the flasks. The mother liquor in the crystallizer was yellowish-brown and slightly unclear at 1300.

AM: July 3; Material has crystallized. ZnO in crystallizer and samples taken at 69°C. and 59°C. ~~[illegible]~~ are contaminated with the light brown ppt. Only the sample taken at 79°C. has yielded white, non-contaminated ZnO. pH of crystallizer reclaim solvent - 7.00 at 25°C.

pH of reclaim solvent from sample filtered at 79°C - 7.02 at 25°C.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 7, 1969 Batch No. 77-1

Solvent Temperature During Solvation: Initial: — Final: 101.1°C.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 3

Solvation Started at: 1030 Finished at: 1145

Agitator Setting Max RPM

Settling Started at: 1145 ; Temperature —

Settling Finished at: 930 July 8 ; Temperature 78°C.

Mother Liquor Pumped to Crystallizer at 930 July 8

Crystallizer Temperature after Pumping was 63°C.

Comments:

Batches 77-1 & 77-2 were filtered to the crystallizer with the Alsop filter using 12— 6 micron discs precoated with 50 gms. of Solka-floc. A sample of the filtrate taken at the filter discharge was light brown in color but was beautifully polished with no apparent solid material suspended therein. However, a sample of the material in the crystallizer 5 minutes after filtering began was turbid, containing suspended brown solids. It appears that the solids form upon oxidation of the filtrate by air.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 7, 1969 Batch No. 77-2

Solvent Temperature During Solvation: Initial: — Final: 215 °F.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 3

Solvation Started at: 1345 Finished at: 1500

Agitator Setting Max RPM

Settling Started at: 1500; Temperature ———

Settling Finished at: 1030 July 8; Temperature 75 °C.

Mother Liquor Pumped to Crystallizer at 1030 July 8

Crystallizer Temperature after Pumping was 63 °C

Comments:

AM of July 9: ZnO crystals precipitated from batches 77-1 & 77-2 were dirtied with the brown ppt. The filtrate sample taken from the filter discharge hose that was beautifully polished originally also precipitated ZnO crystals contaminated with dark brown material.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 8, 1969 Batch No. 78-1

Solvent Temperature During Solvation: Initial: — Final: 215 °F.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 4

Solvation Started at: 1400 Finished at: 1645

Agitator Setting Max RPM

Settling Started at: 1645; Temperature —

Settling Finished at: 1030 July 9; Temperature 76 °C

Mother Liquor Pumped to Crystallizer at 1030 July 9

Crystallizer Temperature after Pumping was —

Comments: 60 gallons of fresh solvent were used for this batch

Batch 78-1 was filtered to the crystallizer using 12 discs of 6 micron retention (no filter aid). A sample was taken from the filter discharge hose. Both the sample and the material in the crystallizer were light brown in color and unmuddied after filtering.

AM; July 10: ZnO crystals in the crystallizer and the small sample are dirtied with the brown material.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 9, 1969 Batch No. 79-1

Solvent Temperature During Solvation: Initial: — Final: 215°C

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.548 Fly Ash Batch No. 4

Solvation Started at: 1400 Finished at: 1545

Agitator Setting Max RPM

Settling Started at: 1545 ; Temperature —

Settling Finished at: 930 July 10 ; Temperature 75°C.

Mother Liquor Pumped to Crystallizer at 930 July 10

Crystallizer Temperature after Pumping was —

Comments: 100 ml. of reagent grade 30% H_2O_2 was added to the reactor along with the fly ash and Zn dust in order to oxidize the collidal ferrous ion in the supernatant liquid to ferric oxide so that it might be retained on the filter media. Foaming of the slurry was noticed on addition of the H_2O_2. A bluish coating on the Monel immersion heaters was noticed after emptying the reactor. The supernatant liquid in the residence tanks was filtered thru 12-6 micron Cuno-Pore discs and the filter discharge was highly polished. However, a brown ppt. started to form in the crystallizer a few minutes after filtering.

AM July 11: ZnO crystals were dirtied to approximately the same degree with Fe_2O_3 as ~~the~~ previous extractions with reclaimed solvent.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 10, 1969 Batch No. 710-1

Solvent Temperature During Solvation: Initial: 140 °F. Final: 215 °F.

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 4

Solvation Started at: 1100 Finished at: 1220

Agitator Setting Max RPM

Settling Started at: 1220 ; Temperature ——

Settling Finished at: 1100 July 11 ; Temperature 83 °C

Mother Liquor Pumped to Crystallizer at 1100 July 11

Crystallizer Temperature after Pumping was ——

Comments: The reclaimed solvent from batch 78-1 (initially fresh solvent) was used to solvent a fly ash batch. The solvent, which had yielded no ZnO ppt., was pumped in toto directly to the reactor from the crystallizer. This solvent had a lighter appearance than the other reclaimed solvent. It was noted that 55 gallons of solvent was reclaimed - the other 5 gallons were retained in the fly ash residue in the drums. 5 gallons of fresh 30% NH_4Cl were added to make up the deficit.

The supernatant liquid from the retention drums was filtered thru 12-micron discs (not precoated with filter aid). The filtrate appeared ighly polished initially in the crystallizer and in a 1 liter sample lask. The filtrate was light brown and about as dark as reclaimed lvent.

M, July 14: ZnO crystals in crystallizer from batch 710-1 are ge, white + monoclinic without a visible trace of Fe_2O_3.

gal. of solvent reclaimed from this batch

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 14, 1969 Batch No. 714 - 1

Solvent Temperature During Solvation: Initial: 110°F. Final: 215°F

Reactor Charge: Gallons Solvent 60 (Fresh) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 4

Solvation Started at: 1215 Finished at: 1430

Agitator Setting Max RPM

Settling Started at: 1430 ; Temperature —

Settling Finished at: 1030 July 15 ; Temperature —

Mother Liquor Pumped to Crystallizer at 1030 July 15

Crystallizer Temperature after Pumping was —

Comments:

All old solvent is being discarded. New solvent is being prepared. The hot water tanks were emptied and flushed with water until the drained water appeared colorless and clear.

Batches 714-1 & 2 were filtered to the crystallizer using 12 discs of 6 micron retention size. The filtrate was highly polished and did not cloud as it cooled in the crystallizer.

AM, July 16: The filtrate from batches 714-1 & 2 have cooled to ambient temperature. Neither ZnO or Fe_2O_3 has crystallized. The filtrate is very clear still.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 14, 1969 Batch No. 714-2

Solvent Temperature During Solvation: Initial: — Final: 215°F

Reactor Charge: Gallons Solvent 60 (Fresh) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 4

Solvation Started at: 1500 Finished at: 1730

Agitator Setting Max RPM

Settling Started at: 1730; Temperature —

Settling Finished at: 1100 July 15; Temperature —

Mother Liquor Pumped to Crystallizer at 1100 July 15

Crystallizer Temperature after Pumping was —

Comments:

The cooled filtrate from batches 714-1 & 714-2 will be reprocessed with fly ash in preparation for a plant material balance.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 15, 1969 Batch No. 715-1

Solvent Temperature During Solvation: Initial: 105°F. Final: 215°F.

Reactor Charge: Gallons Solvent 60 (Fresh) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 4

Solvation Started at: 1100 Finished at: 1245

Agitator Setting Max RPM

Settling Started at: 1245 ; Temperature —

Settling Finished at: 1030 July 16 ; Temperature —

Mother Liquor Pumped to Crystallizer at 1030 July 16

Crystallizer Temperature after Pumping was —

Comments:

The supernatant liquor from batches 715-1 & 715-2 was filtered through 12 - 6 micron Cuno-pore discs to the crystallizer. The filtrate was very clear initially.

1430, July 16: Much Fe_2O_3 is ppt. out in the crystallizer at this point.

900, July 17: ZnO has crystallized along with copious amounts of Fe_2O_3. There exists a layer of Fe_2O_3 floating on the liquid surface.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 15, 1969 Batch No. 715-2

Solvent Temperature During Solvation: Initial: 135° F. Final: 215°C.

Reactor Charge: Gallons Solvent 60 (Fresh) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 5

Solvation Started at: 1425 Finished at: 1550

Agitator Setting Max RPM

Settling Started at: 1550; Temperature —

Settling Finished at: 1100 July 16; Temperature —

Mother Liquor Pumped to Crystallizer at 1100 July 16

Crystallizer Temperature after Pumping was —

Comments:

A small sample of the ~~crystallizer~~ filtrate from batches 715-1 & 2 was taken from the crystallizer after Fe_2O_3 pt. has started but before ZnO crystallization had begun. sample was filtered in the lab thru a 6 micron dium and yielded a very clear filtrate which ppt. an white ZnO crystals.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 16, 1969 Batch No. 716-1

Solvent Temperature During Solvation: Initial: 120°F. Final: 215°F

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 5

Solvation Started at: 1045 Finished at: 1230

Agitator Setting Max RPM

Settling Started at: 1230 ; Temperature ——

Settling Finished at: 1030 July 17; Temperature ——

Mother Liquor Pumped to Crystallizer at 1145 at 68°C. July 17

Crystallizer Temperature after Pumping was ——

Comments: The solvent from batches 714-1 & 2 is being reprocessed with fly ash. 40 gal. of this reclaimed solvent and 20 gallons of fresh solvent made up the solvent of this batch.

The supernatant liquid in the settling drum was pumped with the positive displacement pump to an empty drum and allowed to contact air in the uncovered drum for 1¼ hours. Air was pumped into the drum with the positive displacement pump for about 5 minutes in order to ppt. Fe_2O_3. The supernatant liquid was then filtered thru 6 micron discs to the crystallizer. Although the filtrate from the discharge hose was clear the material in the bath dirtied and ppt. Fe_2O_3 after about 10 minutes.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 16, 1979 Batch No. 716-2

Solvent Temperature During Solvation: Initial: — Final: 215°F

Reactor Charge: Gallons Solvent 60 Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 5

Solvation Started at: 1315 Finished at: 1500

Agitator Setting Max RPM

Settling Started at: 1500; Temperature —

Settling Finished at: 1200 July 17; Temperature —

Mother Liquor Pumped to Crystallizer at 1200 July 17

Crystallizer Temperature after Pumping was —

Comments: 40 gallons of reclaimed solvent from batches 7-14-1 & 2 plus 20 gallons of fresh solvent make up the solvent of this batch.

A small sample of batch 716-2 in the settling drum was filtered hot in the lab thru a 6 micron filter disc a few hours after the solvation reaction. An initial clear filtrate was noted which then started to ppt. ZnO dirtied with Fe_2O_3.

The supernatant liquid was filtered to the crystallizer through 6 micron media. Fe_2O_3 started precipitating out a short while after contact with the air.

AM, July 18: The solvent from batches 716-1 & 2 have crystallized ZnO crystals along with copious amounts of Fe_2O_3.

[redacted]

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 17, 1969 Batch No. 717-1

Solvent Temperature During Solvation: Initial: 150°F Final: 215°F

Reactor Charge: Gallons Solvent 60 (Fresh) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 5

Solvation Started at: 1140 Finished at: 1250

Agitator Setting Max RPM

Settling Started at: 1250; Temperature —

Settling Finished at: 1145 July 18; Temperature 81°C.

Mother Liquor Pumped to Crystallizer at 1145 July 18

Crystallizer Temperature after Pumping was —

Comments:

The reactor and retention drums used for this batch were scrupulously cleaned prior to the making of fresh solvent for this batch in order to determine whether old fly ash residue has an effect on the Fe_2O_3 formation in the crystallizer.

Supernatant liquid from retention drum was filtered thru 6 micron media. The filtrate from the filter discharge hose was very clean and highly polished. After a few minutes retention in the crystallizer, the filtrate started to turn turbid.

AM, July 22: ZnO crystals in crystallizer are contaminated with Fe_2O_3.

[redacted]

ZnO Recovery Pilot Plant Log Sheet

Date: July 22, 1969 Batch No. 722-1

Solvent Temperature During Solvation: Initial: 215°F. Final: 215°F.

Reactor Charge: Gallons Solvent 60 (Fresh) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. $\frac{1}{2}$ from 5, $\frac{1}{2}$ from 6

Solvation Started at: 1330 Finished at: 1400

Agitator Setting Max RPM

Settling Started at: 1400 ; Temperature —

Settling Finished at: 1230 July 23 ; Temperature 69°C. in Zn drums

Mother Liquor Pumped to Crystallizer at 1305 to 1320 July 23

Crystallizer Temperature after Pumping was 57°C.

Comments: Fresh 30 % NH_4Cl was used for this batch. The solvent was heated to 215°F. before adding fly ash. Fly ash (no zinc) was then added and the resulting slurry was agitated 30 minutes. The slurry at 215°F. was then emptied into clean settling drums and settled overnite.

The supernatant liquid from the settling drums was filtered into a clean drum thru 6 micron media (52 gallons of the 60 were recovered thus). 0.948 lbs. of Zn dust was added to this liquid at 1255 and agitated for 5 minutes. The liquor was then filtered to the crystallizer thru fresh 6 micron media. It was noted that a small amount of H_2 gas was released during the Zn reaction. The filtrate from the settling drum was clear but had a green hue. The filtrate into the crystallizer was very clear and was more toward colorless.

On July 24: The ZnO has crystallized without Fe_2O_3 crystallization. ZnO crystals are monoclinic, very white, and much smaller than encountered previously.

[redacted] 47 gal. of solvent were recovered after crystallization

ZnO Recovery Pilot Plant Log Sheet

Date: July 24, 1969 Batch No. 724-1

Solvent Temperature During Solvation: Initial: 215°F. Final: 215°F.

Reactor Charge: Gallons Solvent 60 (Reclaim) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 6

Solvation Started at: 1215 Finished at: 1245

Agitator Setting Max RPM

Settling Started at: 1245 ; Temperature —

Settling Finished at: 1030 July 25 ; Temperature 65°C. in Zn drum

Mother Liquor Pumped to Crystallizer at 1105 to 1120 July 25

Crystallizer Temperature after Pumping was 57°C.

Comments: Reclaimed NH_4Cl solution (solvent that had been used for 2 extractions prior to this one) was used to solvent ZnO in this batch. The solvent was heated to 215°F. and fly ash was added (no Zn dust) and agitated 30 minutes at 215°F; the reactor contents were then drained to the settling drums and settled overnite.

The supernatant liquid was then filtered thru 6 micron media to the zinc agitation drum. Zn dust was added and the contents were agitated 5 minutes (between 1050 and 1055). The liquor was then filtered thru clean 6 micron media to the crystallizer. The initial appearance of the mother liquor in the crystallizer was very clear.

AM, July 28: ZnO has crystallized — no Fe_2O_3 present. ZnO crystals are very white and relatively small.

[redacted]

July 28, 1969

alibration of Kerr-McGee Reactor Vessel (0.34375 Inches of height/gallon)

llons	Inches	Gallons	Inches
1	0.34	41	14.09
2	0.69	42	14.44
3	1.03	43	14.78
4	1.38	44	15,13
5	1.72	45	15,47
6	2.06	46	15,81
7	2.41	47	16.16
8	2.75	48	16,50
9	3.09	49	16,84
10	3.44	50	17.19
11	3.78	51	17.53
12	4.13	52	17.88
13	4.47	53	18,22
14	4.81	54	18.56
15	5,16	55	18.91
16	5,50	56	19,25
17	5,84	57	19.59
18	6,19	58	19.94
19	6,53	59	20.28
20	6.88	60	20.63
21	7,22	61	20.97
22	7,56	62	21,31
23	7,91	63	21,66
24	8,25	64	22.00
25	8.59	65	22,34
26	8,94	66	22.69
27	9.28	67	23.03
28	9,63	68	23,38
29	9.97	69	23.72
30	10,31	70	24.06
31	10,66	71	24.41
32	11.00	72	24.75
33	11,34	73	25,09
34	11.69	74	25,44
35	12.03	75	25,78
36	12,38		
37	12.72		
38	13.06		
39	13,41		
40	13.75		

[redacted]

libration of Kerr-McGee Settling Drums
(0.62170 Inches of height / Gallon)

Gallons	Inches	Gallons	Inches
1	0.62	31	19.27
2	1.24	32	19.89
3	1.87	33	20.52
4	2.49	34	21.14
5	3.11	35	21.76
6	3.73	36	22.38
7	4.35	37	23.00
8	4.97	38	23.62
9	5.60	39	24.25
10	6.22	40	24.87
11	6.84	41	25.49
12	7.46	42	26.11
13	8.08	43	26.73
14	8.70	44	27.35
15	9.33	45	27.98
16	9.95	46	28.60
17	10.57	47	29.22
18	11.19	48	29.84
19	11.81	49	30.46
20	12.43	50	31.09
21	13.06	51	31.71
22	13.68	52	32.33
23	14.30	53	32.95
24	14.92	54	33.57
25	15.54	55	34.19
26	16.16	56	34.82
27	16.79	57	35.44
28	17.41	58	36.06
29	18.03		
30	18.65		

[redacted]

First Batch for Material Balance

ZnO Recovery Pilot Plant Log Sheet

Date: July 28, 1969 Batch No. 728-1

Solvent Temperature During Solvation: Initial: 215°F. Final: 215°F.

Reactor Charge: Gallons Solvent 60 (Reclaim) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 6

Solvation Started at: 1230 Finished at: 1300

Agitator Setting Max. RPM

Settling Started at: 1300 ; Temperature —

Settling Finished at: 1045 July 29 ; Temperature 79°C in sett. drum 65°C. in Zn drum

Mother Liquor Pumped to Crystallizer at 1145 to 1205 July 29

Crystallizer Temperature after Pumping was 56°C.

Zn dust added at 1115 and agitated from 1115 to 1120 (5 minutes)

Comments: 54.5 gallons of satd. solvent pumped to Zn drum. Reclaimed 3% NH_4Cl solvent was heated to 215°F. before adding fly ash. Fly ash was agitated 30 minutes at 215°F. Then the tank contents were drained to the settling drums and settled overnite. The supernatant liquid was filtered to a clean drum thru 6 micron media and agitated for 5 minutes with Zn dust. This liquid was then filtered to the crystallizer thru fresh 6 micron media. The mother liquor in the crystallizer was very clear.

AM July 30; ZnO crystals are very white and uncontaminated with Fe_2O_3.

48 gallons of naked solvent was recovered from the crystallizer. 10 gallons of cold water were used to wash the crystals.

9.00 lbs. of metallic slurry resulted from this batch.

AM, Aug. 5; 33.75 lbs. of wet crystalline product were weighed and a sample [redacted] taken for moisture content.

Second Batch for Material Balance

ZnO Recovery Pilot Plant Log Sheet

Date: July 30, 1969 Batch No. 730-1

Solvent Temperature During Solvation: Initial: 215 °F. Final: 215 °F.

Reactor Charge: Gallons Solvent 60 (Sp.G. 1.087) Pounds Ash 50

Pounds Zinc 0.948 Fly Ash Batch No. 6

Solvation Started at: 1300 Finished at: 1330

Agitator Setting Max RPM

Settling Started at: 1330 ; Temperature —

Settling Finished at: 1140 July 31 ; Temperature 68 °C in Zn drum 82 °C in sett. drum

Mother Liquor Pumped to Crystallizer at 1220 to 1240 July 31

Crystallizer Temperature after Pumping was 60 °C

During the draining of hot fly ash slurry from the reactor ~2 gallons were lost as spillage.

Comments: The 48 gallons of solvent reclaimed from batch 728-1 were pumped to the reactor and 38.5 # of NH_4Cl was added. The reactor contents were diluted to 60 gallons and heated to 215 °F. Fly ash was added and agitated for 30 minutes at 215 °F. then allowed to drain to settling drums for overnite settling. The supernatant liquid was filtered to a clean drum for Zn addition thru 15 micron media. Zn dust was agitated for 5 minutes between 1210 and 1215. 56.5 gallons were filtered into the Zn addition drum.

The liquid was filtered to the crystallizer thru fresh 15 micron media. The mother liquor was very clear.

AM, August 1: ZnO crystals are very white and uncontaminated with Fe_2O_3.

49 gallons of naked solvent was recovered from the crystallizer. 10 gallons of cold water were used to wash the crystals, Sp.G. of reclaimed solvent was 1.096

[redacted] 8.75 lbs. of metallic slurry resulted from this batch.

[redacted]

AM, Aug 5: 27.00 lbs. of wet crystalline product were weighed and a sample was taken for moisture analysis

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

August 27, 1969

Kerr-McGee Chemical Corporation
Kerr-McGee Building
Oklahoma City, Oklahoma 73102

Attention: Dr. L. E. Craig
Vice-President - Manufacturing

Subject: Final Technical Report, Project A-1153
Zinc Oxide Recovery Process

Gentlemen:

In a previous study it was found that zinc oxide could be recovered from electric furnace flue dust in appreciable quantities, particularly in the case of reclaim operations involving considerable quantities of galvanized scrap. Hot ammonium chloride is used as a solvent; the zinc oxide is extracted from residuals by the hot solvent, then crystallizes upon cooling. Lead oxide is extracted simultaneously, as lead chloride, while copper is extracted as an ammonium complex. Most of the lead chloride deposits with the zinc oxide, upon cooling, while the copper remains in solution.

A typical analysis of flue dust from a local source indicated that the theoretical yield from one ton of flue dust would be:

Zinc oxide	792.8 lb.
Lead, metallic	100.6 lb.
Copper, metallic	minor
Iron oxide, magnetic	734.8 lb.

The lead would be obtained in metallic form by displacement with zinc; the zinc oxide yield would then be increased by an equivalent amount; namely, 41.5 lb. The working solvent for processing 1 ton of flue dust was estimated as consisting of:

Ammonium chloride	5,940 lb.
Water	1,884 gal.

The laboratory studies had indicated that 90% yields could be expected on both zinc oxide recovery and solvent recovery, with possible increases.

The present study was inaugurated for the purposes of scaling up the extraction process to pilot plant proportions and supplementing the previous laboratory studies to obtain data pertinent to commercial application of the process. Unforeseen problems that arose in setting up the pilot plant and in operating the equipment made it impossible to complete all of the proposed program. This report details the procedures followed and results obtained in the work that was completed.

I. EXPERIMENTAL PROGRAM, LABORATORY

A. Crystal habit, particle size distribution and chemical composition of zinc oxide obtained in this process

The crystals of zinc oxide that form upon cooling the ammonium chloride solvent are glassy, acicular, and range in size up to 3/8 inch in length. Analysis of a sample produced in the laboratory showed an ammonium chloride content of approximately 2 percent. Washing with cold water reduces the chloride content, but at the same time the crystals disintegrate to a white, powdery form. Apparently, the ammonium chloride is occluded in the crystal in such a manner that, upon being dissolved out, it causes the crystal to lose its structural integrity.

The crystals are fairly friable and can be easily ground to fine form. The resulting powder, extracted with hot water, shows a chloride content of less than 0.2 percent. For most applications (paint pigments, rubber compounding, etc.) this level of ammonium chloride would not be objectionable; if the zinc oxide is to be used for production of zinc chloride (e.g., Pyrosote), a larger ammonium chloride content would be acceptable.

No X-ray diffraction or electron microscopy studies were made.

B. Composition of the residue, iron oxide

Due to the lack of time, no work was done on this item.

C. Phase relationships of the system, $ZnO-NH_4Cl-NH_4OH-H_2O$

Solutions were prepared by dissolving specific quantities of ammonium chloride in 100 ml. water, then saturating with zinc oxide at various constant temperature levels. As shown in Figure 1, uniformity of solution composition was achieved by refluxing the water that evaporated and by constant agitation of the solution. At intervals, aliquots were withdrawn, discharged into hydrochloric acid solution, heated to boiling and titrated with standard potassium ferrocyanide solution. Results were calculated as weight of zinc oxide dissolved by the 100 ml. water to which the ammonium chloride had been added. These results are presented in Table I.

In a subsequent set of experiments, ammonium hydroxide was added to the ammonium chloride solutions, above, and the solubility of zinc oxide in the resulting solution was determined at various temperatures. In each case, the solubility was appreciable increased throughout the temperature range, although not linearly. Results are included in Table I.

For the purposes of the subject process, it is apparent that a 30 percent solution of ammonium chloride provides the steepest solubility <u>vs</u> temperature curve, and that the steepest portion of this curve lies between 40° and 90° C. (104° and 194° F.). Thus, a 30 percent solution would be the most effective solvent for zinc oxide, when used at 194° F., in the leaching of flue dust. It would release a maximum portion of this zinc oxide, by crystallization, when cooled to 104° F. or lower (in the pilot plant study, the lower temperature was about 60° and the upper, about 215° F.).

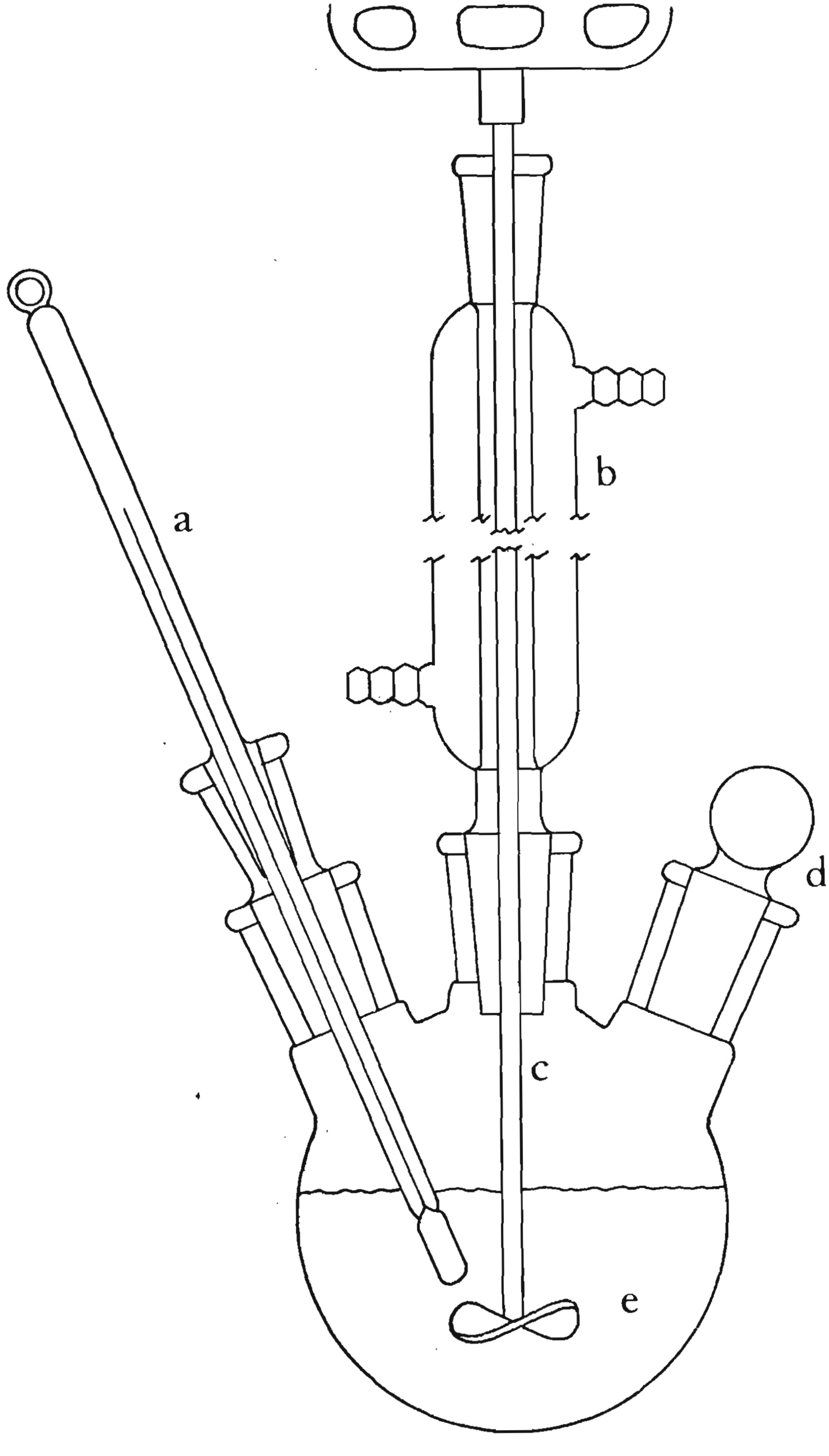

Figure 1. Apparatus for Solubility Equilibrium Measurements

a. Thermometer, b. Condenser, c. Agitator, d. Sample Port, e. Saturated Solution

TABLE I

Solubility of Zinc Oxide in Ammonium Chloride-Ammonium Hydroxide Solutions

Temperature, °C.		20	40	60	70	80	90
Solvent Composition (g NH_4 Cl) / 100 ml H_2O	(ml NH_4OH) / 100 ml H_2O	(Solubility (g.ZnO/100 ml. H_2O)					
10	0	0.4	0.7	1.3	--	1.8	--
15	0	0.8	1.6	2.6	--	3.5	--
20	0	0.8	1.6	4.6	--	7.5	--
25	0	1.2	2.5	6.0	10.2	11.0	11.6
30	0	1.0	2.3	5.0	8.4	13.2	14.6
20	4	--	--	5.9	9.7	11.4	--
25	4	--	--	6.7	11.9	13.3	--
30	4	--	--	6.2	9.3	16.2	--
20	8	--	--	7.6	11.2	13.3	--
25	8	--	--	9.0	13.7	14.4	--
30	8	--	--	7.4	13.6	17.5	--

D. Preliminary evaluation of the chemical resistance of plant construction materials

At the outset of the pilot plant operation, we had planned to immerse test spools of various candidate metals in the processor where they would be continually exposed to fresh and recycled solvent at 215° F. We did not follow through on this plan for two reasons. First, we received a copy of International Nickel Company Corrosion Engineering Bulletin CEB-3, which reports (Table 32, p. 28) the corrosion rates of Monel alloy 400, Nickel, Inconel alloy 600, Ni-Resist (Type 1) and cast iron in evaporation for ammonium chloride from 28 to 40 percent at a temperature of 216° F. The duration of the test was 762 hours, which greatly exceeded any exposure time we would have been able to achieve.

Second, while we had planned to include some stainless steels in our test, laboratory experience prior to the pilot plant operation showed an unexpected lack of resistance, even on the part of 316 SS. Had spools containing these, and possibly other less noble metals, been exposed in the processor, it is quite likely that our problem with iron oxide (later) would have been still harder to track down.

In lieu of the intended studies, the data given by INC is shown in Table II. In addition, reference is made to the more extensive data provided by INC under cover of March 26, 1969 and included as an attachment to our Monthly Report No. 1.

TABLE II

Plant Corrosion Test in Evaporation of Ammonium Chloride From 28 to 40 Per Cent NH_4Cl

Test spool immersed in liquor

Temperature: 102° C. (216° F.)

Duration of test: 762 hr.

Material	Corrosion Rate	
	mdd.	ipy.
Monel alloy 400	73	0.012
Nickel 1	52	0.0084
Inconel alloy 600	3	0.0005*
Ni-Resist (type 1)	63	0.012
Cast Iron	1780	0.36

*Pitted to maximum depth of 0.006 inch

II. EXPERIMENTAL PROGRAM, PILOT PLANT

A. Analytical procedures

As a means of monitoring the performance of the pilot plant, the laboratory prepared the necessary reagents and apparatus to analyze the solvent for both ammonium ion (Kjeldahl method) and chloride ion (thiocyanate method). Analysis for zinc oxide was continued, using the method previously cited. The laboratory of the Kerr-McGee plant at Powder Springs analyzed all batches of flue dust for zinc, lead, copper and iron.

While we were waiting for the pilot plant installation to be completed, several laboratory extractions were made on one-pound quantities of flue dust. In one experiment, 80% of the ZnO was recovered; the solvent recovery was not determined. Two experiments gave ZnO recovery of 70% and solvent recovery of 80%; a fourth experiment gave ZnO recovery of 58% and solvent recovery of 83%. In all of these runs, there was an indeterminate factor of solvent evaporation during the filtering step, which is absent in the pilot plant. The laboratory uses vacuum filtration; consequently, as the hot solvent reaches the low pressure side of the filter, its rate of evaporation increases, and it is quickly cooled to room temperature. This causes rapid crystallization of the zinc oxide, sometimes within the pores of the filter; this, in turn, causes an even greater drop in pressure, with still more rapid cooling. Under these circumstances, the laboratory procedure is hardly comparable with the pilot plant operation, in which a filter press is used.

B. Equipment

The plant consisted of the following equipment:

1. Solvent Preheaters. Two 50-gallon, glass lined, gas fired hot water heaters were intended to bring the 30% ammonium chloride solution up to process temperature. As it turned out, these heaters were conventionally thermostated and cut out at about 165° F. To have replaced the thermostats with higher range units would have entailed additional time losses, and they could not be safely operated without thermostats; hence, it was necessary to use the processor for final heating of the solvent (to 215° F.). The heaters were furnished with vinyl fittings; piping for the plant was of flexible Hypalon.

2. Processor. A 100-gallon steel tank was lined with Hypalon and provided with a Lightning mixer with Monel agitator. The vessel was calibrated in gallons <u>vs.</u> inches of liquid level. It was mounted on a 4-foot high platform; a 2-inch shut-off valve in the bottom provided gravity discharge into a settling drum at the end of the dissolving process. Initially, the processor, although provided with a lid, was not insulated, as it was anticipated that delivery to the vessel would be at process temperature and that the heaters would have only to hold that temperature. However, heat loss through the side walls was considerable, requiring hours to bring the solvent up to temperature; a 2-inch layer of polystyrene foam was required to contain the heat effectively.

3. Standard 55-gallon steel drums were lined with Hypalon and insulated with 2-inch built up layers of polystyrene foam in $\frac{1}{2}$-inch roll form. Lids were fabricated by laminating two 1 inch thick circles of rigid foam, one cut to fit just inside the drum, the other extending over the rim. Bottoms were insulated with the same material.

These drums served the purpose of holding the process mixture long enough to permit settling of the iron oxide, but at high enough temperature to prevent crystallization of the zinc oxide. Temperature drop in these drums was of the order of 2° to 3° C. (3.6° to 5.4° F.) per hour, which was well within tolerable limits.

4. Filter Press. A Cuno 12-disc portable filter press, of Monel construction, served to pump and filter the decantate from the settling drums into the crystallizing vat. The decantate was withdrawn from the drum by lowering into it a hose attached to the low pressure side of the filter press pump; this hose terminated at its take-up end in a 5-inch fritted polypropylene filter disc, intended to guard against pick up of sludge from the bottom of the drum.

5. Crystallizing Vat. A 4-foot by 8-foot vat, 2 feet deep, was constructed of $\frac{1}{2}$-inch indoor-outdoor plywood, supported on bottom and sides by 2 x 4 inch wood framing. All corner joints were caulked with epoxy compound, which was also used to cover all countersunk screws on the interior surfaces. The interior and the top flange were painted with two coats of gray epoxy enamel.

The hot filtrate from the filter press was discharged into the vat and cooled by evaporation. At the end of the cooling process, a considerable quantity of zinc oxide crystals had collected on the floor of the vat. These were scooped up and deposited onto a cotton drill screen, supported on wooden cross bars, resting on the top flange of the vat.

When the supernatant liquor had drained from the crystals, the solvent was pumped from the crystallizing vat back into the preheaters or into solvent storage drums. The crystals were then washed, first with cool water, then with hot water.

Figure 2 is a photograph of the pilot plant, showing the features described above.

C. Operation

It was intended that the zinc oxide extraction would be conducted according to two procedures and that materials balances would be determined for both procedures.

Procedure I: The flue dust would be digested in the hot 30% ammonium chloride solution. Sufficient zinc metal dust to displace the lead and copper as metals would be added together with the flue dust. There would be no effort to recover the lead and copper; these, together with the iron oxide, would be discarded. The filtered decantate from the settling drums would contain only hot zinc oxide-ammonium chloride solution, from which the zinc oxide, the sole product, would crystallize upon cooling.

Procedure II: The flue dust would be digested in the hot ammonium chloride solution, followed by settling and filtration. While the solution was sufficiently hot that no crystallization would occur, zinc metal dust would be added to displace the copper and lead. These would be separated from the solution by settling and filtration as a metallic mixture of lead, some zinc and a trace of copper. The zinc oxide would be recovered by crystallization from the second filtrate.

The study commenced with Procedure I.

D. Procedures and Results

On the basis of preliminary experiments, the standard batch charge was adopted as:

Gallons solvent:	60
Pounds flue dust:	50
Pounds zinc dust:	0.948

The charge entered the processor at about 60° C. (140° F.) and was brought up to ca 101.7° C. (213° F.) over a period of about $1\frac{1}{2}$ hours. This was sufficient to complete dissolution of the zinc oxide; the mix was then dumped into settling drums (which might contain residue from previous batches). A settling time of $2\frac{1}{4}$ - $2\frac{1}{2}$ hours was sufficient, after which the decantate was filtered into the crystallization vat.

A second sample could be processed while the proceeding one was settling, and filtrates from a number of batches could be accumulated in the crystallization vat. Crystals could be scooped into the screen and drained, then removed to another position for washing.

The first batch was run on June 16, 1969. Solvation was started at 11:20 A.M.; the filtrate went into the crystallizer at 3:00 P.M. Reddish brown material was noted on the zinc oxide crystals that day and the next and were identified as ferric oxide. The source of iron was through to be a mild steel tee joint in the solvent line, as the iron oxide of the flue dust does not contaminate the solvent. The tee was replaced by a vinyl tee on June 17. When the problem continued on subsequent days, a nickel-plated impeller shaft was replaced by a monel unit.

Throughout the period that found us battling the iron oxide problem, it was evident that the process was yielding a good quality and quantity of zinc oxide and that the ferrous contamination was no more than 0.2%. This was sufficient, however, to seriously affect the usefulness of the product for certain purposes. The density and other properties of the ferric oxide were such that it was not readily separable from the zinc oxide.

Attempts were made to eliminate the iron oxide by reduction of the filter pore size to 6 microns. It soon became apparent, however, that the iron was present in either solution or colloidal form. It did not show up in the fresh filtrate, but began to form as a yellowish brown skin on the surface of the liquor in the crystallizer. Once formed, the iron oxide could be removed by reheating and refiltering the zinc oxide-solvent mixture.

Taking a cue from this observation, we attempted to convert the iron in the solvent to ferric oxide, prior to filtering, by aeration or by addition of hydrogen peroxide. These measures failed.

We discarded all old solvent, as contaminated, but the fresh solvent soon showed the same effect. By now it had become evident, by elimination, that the source of contamination must be the flue dust. If so, then the lower valence iron must either be present in the flue dust, probably as metallic iron, converted to ferrous chloride in the processor, or be produced in the processor by reduction of Fe_3O_4.

No metallic iron had, as yet, been experienced in laboratory experiments, nor would it be expected to be present in a flue dust produced under the extreme conditions of an electric furnace. It appeared, then, that the ferrous contamination was arising by reduction in the processor; e. g.,

$$Zn^o + 2H^+ \rightarrow Zn^{++} + 2[H^o] \tag{1}$$

$$Zn^o + 2NH_4^+ \rightarrow Zn^{++} + 2NH_3 + 2[H^o] \tag{2}$$

$$Fe^{+++} + [H^o] \rightarrow Fe^{++} + H^+ \tag{3}$$

$$H^+ + NH_3 \rightarrow NH_4^+ \tag{4}$$

$$4\ Fe^{++} + O_2^o + 8\ OH^- + 2\ H_2O \rightarrow 4\ Fe\ (OH)_3\downarrow \tag{5}$$

Equations 1 and 2 show how either hydrogen ion or ammonium ion (from water or ammonium chloride) might react with metallic zinc to produce nascent (active, monatomic) hydrogen. Equation 3 shows how this hydrogen reacts with ferric (higher valence) iron to produce the ferrous (lower valence) iron, while equation 4 shows the resulting hydrogen ion reacting with ammonia to reform ammonium ion. Equation 5 shows how oxygen of the air converts the ferrous ion into reddish-brown, insoluble ferric hydroxide. Proof of this hypothesis was demonstrated by omitting zinc dust from the processor, as required by Procedure 1, and going, instead, to Procedure 2; the iron oxide problem disappeared immediately. It did not reappear, even in the reuse of old, previously contaminated solvent.

We were thus brought to the conclusion that Procedure 1 is not feasible for this process, whereas Procedure 2, in addition to providing lead and copper in recoverable form, yields a product zinc oxide entirely free of iron oxide. Figure 3.

E. Materials Balance

After the exhaustive work on iron oxide contamination, remaining funds were sufficient only for a preliminary evaluation of the materials balances of Procedure 2. Two runs were made for this purpose; the calculations of the results are given in detail on pages 36 and 37 of the pilot plant notebook. These results are shown in Table III.

TABLE III

Recovery of Zinc Oxide, Solvent, and Metals by Procedure 2

Materials Balance Run No:	-1-	-2-
Solvent Recovery, % by volume (1)	80.0	81.7
Ammonium Chloride Recovery, % by wt. (2)	80.0	93.8
Zinc Oxide Recovery, % by wt. (3)	96.3	73.6
Lead and Copper Recovery, % by wt. (4)	~100.0	~100.0

Remarks

1. Solvent recovery was limited in these studies to what could be realized from a $2\frac{1}{2}$ hour settling time, followed by filtration of the decantate. The undecanted slurry of (primarily) iron oxide was still quite wet; however, separation of further liquor from this slurry by filtration would have placed a very heavy burden on the filter press. A laboratory scale study of the slurry discarded in Run No. 1, however, showed that approximately 60 percent of the slurry liquor could be recovered by centrifugation; presumably, an extended settling period--e.g., 24 hours, would accomplish the same result. Our studies have demonstrated the feasibility of holding a satisfactory settling temperature for 12-15 hours with 2 inches of polystyrene foam insulation.

By extending the settling time, or by centrifugation, it should be possible to reduce the solvent loss by 60 percent, making solvent recovery 92% and 92.7%, respectively, for the two runs.

2. Ammonium Chloride loss in Run No. 2 was appreciably lower than in Run No. 1, as a result of cooperative action of three factors; a slightly lower solvent volume loss, a concencentration factor (in at 26.6%, out at 30.3%), and improved separation of slurry liquor. Both losses should be reducible by about 60% by centrifugation or extended settling.

3. By contrast, the zinc oxide recovery was reduced by action of two factors; the lower initial solvent strength, which was not discovered until the run was under way and the retention of ZnO in the fresh make-up solvent. The latter loss does not occur in recycled solvent, which is already saturated with ZnO from previous runs.

The value of 96.3% recovery in Run No. 1 is apparently erroneously high, for addition of the ZnO recoverable by centrifugation, plus that in the unrecoverable slurry liquor, would put this value over 100%. A minor source of error would be approximately 2% by weight of occluded ammonium chloride. The major error probably is in taking a sample of wet crystals for moisture determination; a representative sample is difficult to obtain. In any event, the recovery of ZnO in Run No. 1 (correct solvent concentration) was very encouraging.

4. There was no attempt at precision in determining the lead-copper recovery. Obviously, some unreacted zinc remains, there is some oxide formation, etc. Only by quantitative analysis can the recovery of these metals be accurately assayed; however, it is also encouragingly high.

Conclusions

1. Because of unforeseen difficulties, it was not possible to present a complete pilot plant study; however, even the incomplete study indicates a high degree of feasibility for the process.

2. Simultaneous extraction of zinc oxide and precipitation of lead and copper (via zinc dust) results in contamination of the product with iron oxide.

3. Extraction of zinc oxide by hot, 30% ammonium chloride solution, followed by settling and filtration, then by addition of zinc metal dust to precipitate lead and copper, results in a white, acicular crystalline product of apparently high quality.

4. The product may contain up to 2% of occluded ammonium chloride, extractable with water after grinding.

5. With improved separation of liquor from residue, zinc oxide recoveries in excess of 95% and solvent recoveries in excess of 90% are to be expected.

Respectfully submitted,

[redacted]

W. H. Burrows
Project Director

WHB:sm