PRELIMINARY INVESTIGATION

OF

THE TREATMENT OF LEAD AND ZINC CARBONATE ORES

WITH

SODIUM HYDRATE

FOR

THE NEVADA STATE BUREAU OF MINES

JAY A. CARPENTER, DIRECTOR

BY

R. L. MIDDLEKAUFF

DECEMBER 1942

Mr. Jay A. Carpenter, Director
Nevada State Bureau of Mines
Reno, Nevada

Dear Sir:

On October 12, 1942, you requested that the writer investigate the feasibility of your plan to utilize sodium hydrate to treat lead and zinc carbonate ores. The enclosed report is based upon experimental work done by the writer, under your direction in the laboratories of the Mackay School of Mines.

Grateful aknowledgment is extended by the writer to Professor William I. Smythe of the University of Nevada for his sincere cooperation and help, without which the investigation would have been practically impossible.

Reno, Nevada

December 20, 1942

Respectfully submitted,

Robert L. Middlekauff

Robert L. Middlekauff

CONCLUSIONS

Ores containing lead and zinc, alone or together, in the form of carbonates, are completely soluble in sodium hydrate solutions (aqueous solutions).

Failure to dissolve the lead and/or zinc minerals in ore is due to two things: Incorrect hydrate strength or dilution ratios; and attempts to dissolve lead and zinc minerals that are of such chemical composition no reaction is possible in the first place. For example sulfides, they definitly are not soluble in sodium hydrate. It would be useless to attempt to treat a sulfide ore with hydrate solution.

Examination of tails from tests that failed to yield extraction of lead showed that the lead was present as galena. For which mineral no claim is made that hydrate extraction is feasable.

The hydrate treatment results in general in a reduction in weight of the ore to tail stage. this results in a great benificiation of the contained product in the case of insoluble constituents. The gross weight of the tail in one case was less than one half of the weight of the heads. This meant that insoluble mineral percent was more than doubled by the treatment.

No generalization as to correct strength hydrate nor ratio of dilution is possible. For example consider the mineral Zincite (ZnO) no consumption of hydrate would result if this mineral were treated hydrate; other than the simple mechanical loss due to imperfect filtering of the tails.

Zn + Pb both more soluble in NaOH by hot then Na₂CO₃ fouling not a serious problem

The best temperature is 30° C considering maximum solubility in connection with lowest dilution ratio and optimum hydrate strength. However it would not be worth the cost to botherheating solutions above room temp. 20° C to obtain the ideal of 30°

= 86°F

High temp speeds up SiO₃ reactions but - decrease sol of Zn in NaOH

Hot solutions are absolutely not desirable. They lower the solubility of lead and zinc as plumbates and zincates. Cold solutions (5° or more below 20° C) are not desirable they cause a decrease in the solubility, of lead and zinc salts.

→ = 68°F

Fortunately the temperature of 20° C is ideal considering that no special equipment is needed and it is a comfortable working tmeperature for the workman.

a hydrate sol of 38 % NaOH will give the greatest dissolution of Zn - but if Zn is present a carbonate due allowance must be made for the reaction $ZnCO_3 + 2NaOH \rightarrow Zn(OH)_2 + Na_2CO_3$ in other words after consumed NaOH is subtracted from total strength 38 % is the amt that should be left to dissolve a max wt Zn with the lowest ratio of ore to sol by weight. 38 % a critical point solubility of Zn falls off Rapidly at higher strengths NaOH.

It is obvious that there must be sufficient hydrate present to "wet" the ore. Therefore for example a 1% Zn ore would require more than a fraction of a ton of 38% hydrate for mechanical reasons alone.

38% NaOH Solution.

%
Zn

45%
40%
35%
30%
25%
20%
15%
10%
5%
0

1 2 3 4 5 6 7 8 9 10 11 12 13 14

Minimum Tons of hydrate required
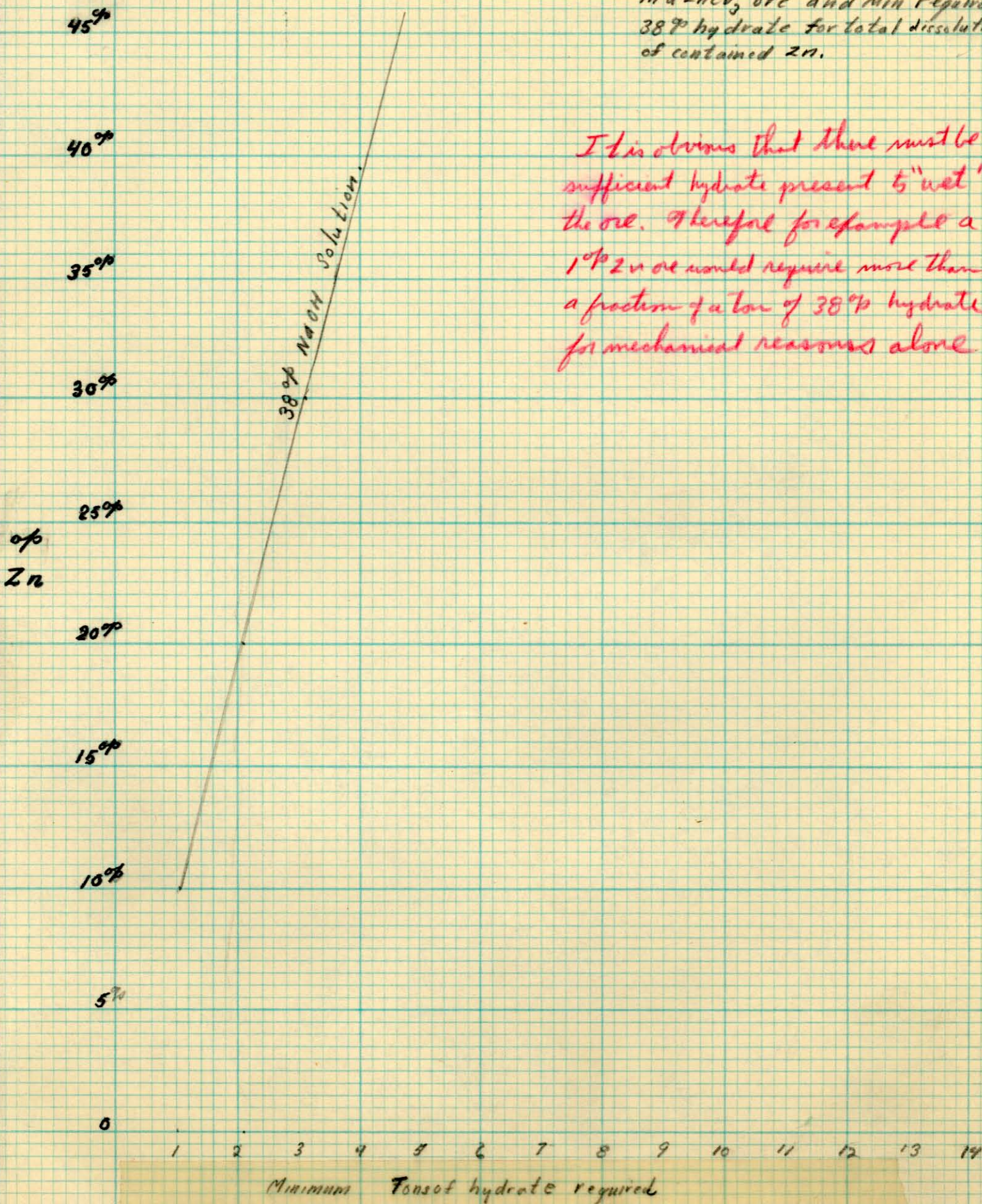
EMPIRICAL METHOD OF CALCULATING HYDRATE CONSUMPTION.

(1) Calculate the Pb, Zn, NaOH, and Na_2CO_3 titres of the standard HNO_3 used for titration. (Note-use HNO_3 only for titrations).

(2) Divide weight of Pb in hydrate sample by the Pb titre of the standard acid. This will yield the number of cubic centimeters of acid consumed by the $Pb(OH)_2$

(3) Do the same as in (2) for Zn.

(4) Add the cc's of std. acid required for Pb to those required for Zn.

(5) Subtract the total found in (4) from the cc's required to titrate from a phenolphthalein end point to a methyl red end point. The difference found will equal the cc's required to titrate one half of the Na_2CO_3.

(6) Double the difference found in (5), multiply by the Na_2CO_3 titre of the std. acid and divide by the weight of solution taken for analysis x 100 = % Na_2CO_3 in the hydrate.

(7) Subtract the difference found in (5) from the cc's of std. acid required to reach a phenolphthalein end point. This will give the cc's of std. acid required to react with the NaOH present in the sample. Multiply the number of cc's found by the NaOH titre of the std.acid. divide by the weight of sample taken for analysis x 100 = the % NaOH in hydrate.

(8)   From the weight of NaOH in the head solution subtract the weight of NaOH found in the pregnant solution (the latter found from (7)). This will yield the total NaOH consumption.

(9)   Subtract the weight of Na_2CO_3 in the head solution from the weight of Na_2CO_3 found in the pregnant solution (the latter calculated from (6)). This will give weight of Na_2CO_3 produced in processing the ore.

(10) Convert the weight of Na_2CO_3 found in (9) to NaOH. From the total consumption of NaOH (calculated in (8)) subtract NaOH equivalent of the Na_2CO_3. This will yield the amount of NaOH consumed by reactions other than the carbonate reactions. This last figure will include loss in tail, silicate consumption, aluminate consumption, etc. of NaOH.

NOTE Steps (9) & (10) in the method of calculation fail completely whenever the amount of Na_2CO_3 present in a test exceeds the solubility of Na_2CO_3 permissible in given strength hydrate solution. This failure occurs in two ways or in a combination of two ways: First if the Na_2CO_3 in the head solution is present in a greater amount than to permit a true solution. Second if the Na_2CO_3, produced by replacement of $ZnCO_3$ and/or $PbCO_3$, exceeds that amount that will dissolve in the pregnant solution.

Grams NaOH per 100 cc. solution

Grams of Zn(OH)$_2$ plotted
against grams of NaOH per
100 grams of sat. solution.
Data - Goudriaan, 1919.

Grams of
Zn(OH)$_2$

Grams of NaOH per 100 grams sat. sol.

Form No. 513 — 20 Squares to Inch
SCHWABACHER-FREY CO. · SAN FRANCISCO, LOS ANGELES

COMPLETE SAMPLE CHEMICAL CALCULATIONS ON 'HOOSIER' ORE TEST

HEAD SAMPLE

Standard solution potassium ferocyanide   Zn titre
one c.c. = .0050149 grams zinc.

$$\frac{14.90 \text{ cc's x } .005015 \text{ g./cc.}}{.5 \text{ gram sample}} \text{ x } 100 = 14.94\% \text{ Zinc}$$

Standard sol. Lead molybdate   Pb titre = .00513 g.

$$\frac{16.38 \text{ cc's x } .00513 \text{ g./cc.}}{.5 \text{ gram sample}} \text{ x } 100 = 16.82\% \text{ Lead}$$

SODIUM HYDRATE HEAD SOLUTION

Standard HNO_3 CaO titre = .005 grams

$$.005 \text{ x } \frac{2NaOH}{CaO} = .005 \text{ x } \frac{80.02}{56.08} = .00713 \text{ grams NaOH}$$

$$.005 \text{ x } \frac{Na_2CO_3}{CaO} = .005 \text{ x } \frac{106.}{56.08} = .00945 \text{ grams } Na_2CO_3$$

$$.005 \text{ x } \frac{Zn}{CaO} = .005 \text{ x } \frac{65.38}{56.08} = .00582 \text{ grams Zn}$$

$$.005 \text{ x } \frac{Pb}{CaO} = .005 \text{ x } \frac{207.21}{56.08} = .01845 \text{ grams Pb}$$

- -

Standard acid required to reach a phenolphthalein
end point = 1010 cc. total to methyl red end pt. = 1040 cc.

1040 - 1010 = 30 cc. for 1/2 the Na_2CO_3 or 60 cc.total

$$\frac{60 \text{ cc. x } .00945 \text{ g.}Na_2CO_3/cc.}{10 \text{ cc. sample x sp.gr. } 1.4379} \text{ x } 2000 = 78.9 \text{ lb } Na_2CO_3/ton$$

$$78.9 \div 2000 \text{ x } 100 = 3.95\% \text{ } Na_2CO_3$$

1010 cc. - 30 cc. = 980 cc. std. acid for the NaOH.

$$\frac{980 \text{ cc. x .00713 g NaOH/cc. x 2000}}{10 \text{ cc x sp.gr. } 1.4379} = 974 \text{ lb.NaOH/ton sol.}$$

$$984 \text{ x } 100 \div 2000 \qquad\qquad = 48.7\% \text{ NaOH}$$

To 400 cc. of the 48.7% NaOH. 400 cc. of H_2O added.

400 cc. of hydrate x sp.gr. 1.4379 = 575.2 grams

575.2 grams x $\dfrac{974}{2000}$ = 280.12 grams of dry NaOH

$$\frac{280.12}{575.2 + 400 \text{ gms. } H_2O} \text{ x } 100 = 28.75 \% \text{ Hydrate, actual}$$

strength of hydrate used in the ore test. 575 lb./ton of sol.
not including the wt. of NaCl or Na_2CO_3, NaOH only

PREGNANT HYDRATE SOLUTION

Specific gravity = 1.343+

$$\frac{38.2 \text{ cc. x .0050149 g.Zn/cc.}}{10 \text{ cc. sample x sp.gr. } 1.34} \text{ x } 100 = 1.426\% \text{ Zinc.}$$

727. cc. of pregnant hydrate recovered from test.

$$\frac{727.\text{cc. x } 1.343 \text{ x } 1.426\% \text{ Zn}}{100 \text{ g. ore x } 14.94\% \text{ Zn}} \text{ x } 100 = 93.2\% \text{ recovery of Zn.}$$

$$\frac{43.6 \text{ cc x .00513 g Pb/cc.}}{10 \text{ cc. x } 1.34} \text{ x } 100 = 1.67\% \text{ lead}$$

$$\frac{727 \text{ cc. x } 1.343 \text{ x } 1.67\% \text{ Pb}}{100 \text{ g. ore x } 16.82\% \text{ Pb}} \text{ x } 100 = 96.96\% \text{ recovery of Pb}$$

NaOH and Na_2CO_3 in pregnant hydrate.

501 cc of std acid required to reach Phenophthalene end pt.
552 cc of std " " " " methyl red " "

$$\frac{10 \text{ cc sample x } 1.343 \text{sp.gr. x } 1.67\% \text{Pb}}{0.01845(\text{Pb titre of acid})} = 12.17 \text{cc.acid to Pb.}$$

$$\frac{10 \text{ cc sample} \times 1.343 \times 1.42\% \text{ Zn}}{.00582 \text{ g Zn/cc. (Std.Acid Zn Titre)}} = 32.78 \text{ cc acid to Zn}$$

12.17 cc to Pb + 32.78 cc to Zn = 44.95 cc total acid

to react with lead and zinc hydroxides.

552 cc. acid to Methyl red end pt.
-501 cc. "   " Pheno.   " ".

51. cc. required for Pb + Zn + 1/2 of the Na_2CO_3
- 44.95 cc. for Pb + Zn

     6.05 cc for 1/2 of the Na_2CO_3.
x   2

  12.1 cc for total Na_2CO_3

$$\frac{12.1 \times .00945 \ (Na_2CO_3 \text{ titre})}{10 \text{ cc} \times 1.343 \text{ sp.gr.}} \times 100 = .851\% \ Na_2CO_3 \text{ in preg sol}$$

or .851% × 2000   = 17.02 lb. Na_2CO_3/ton sol

501.00 cc required for NaOH + 1/2 of the Na_2CO_3
  -6.05 cc   "   "   1/2 "   "   "

494.95 cc   "   "   NaOH

$$\frac{494.95 \times .00713 \ (NaOH \text{ titre})}{10 \text{ cc} \times 1.343} \times 100 = 26.3\% \ NaOH$$

                                  or = 526 lb " /ton of sol.

727 cc. pregnant hydrate recovered × 1.3433 sp.gr.

x 26.7% NaOH = 256.84 grams NaOH (dry wt.) recovered

575.2 g. head × 48.7% NaOH = 280.6 g NaOH in head (dry wt)

280.6 - 256.8 = 23.8 grams NaOH consumed, this includes

tail loss, silicates, carbonates, aluminates. etc.
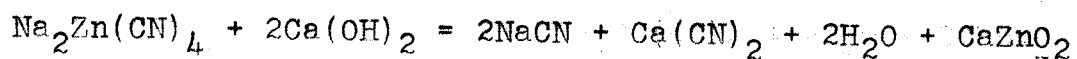
23.8 ÷ 280.6 × 100 = 8.5% of NaOH in heads lost.

23.8 /100 = X/2000   X = 276 Lbs. dry NaOH consumed/ton ore.

qualitatively tested for lead and zinc, with positive results
for both metals. Exactly what chemical reaction occurs was
not determined. The writer believes that the reaction is
probably as follows:

$$Na_2Zn(OH)_4 + Ca(OH)_2 = 2NaOH + 2H_2O + CaZnO_2$$

This reaction proposed by the writer parallels one in the
chemistry of precious metal cyanidation. The double cyanide
salt, $K_2Zn(CN)_4$ or $Na_2Zn(CN)_4$, reacts with $Ca(OH)_2$ this way:

$$Na_2Zn(CN)_4 + 2Ca(OH)_2 = 2NaCN + Ca(CN)_2 + 2H_2O + CaZnO_2$$

The successful regeneration of the sodium cyanide salt depends
on the insolubility of the calcium zincate formed. The irrever-
sibility of the reaction depends on the calcium zincate being
precipitated.

The writer did not feel that it was within the scope
of this investigation to experiment with the effects of calcium
hydroxide. There is considerable technical literature available
written about the subject of the solubility of calcium salts.
The explanations given are not entirely satisfactory. The
writer did however make a careful study of the proposition to
regenerate NaOH from hydrate solutions barren in lead and zinc.
It is entirely feasable to regenerate hydrate solutions if the
lead and or zinc has been previously removed by electrolysis
or chemical means. Care should be used not to introduce an

DATA SUMMARY OF 'HOOSIER' ORE TEST

<u>Ore</u>	100 gm.	16.82% Pb	14.94% Zn	
Hydrate on	975.2 g.	0.	0.	28.75% NaOH
Hydrate off	727 cc 976.6 g.	1.67%	1.42%	26.3 % NaOH
<u>Tails</u>(dry)	78. g.	.65%	1.36%	-- -

Treatment

    Ore stage pulverized to pass - 100 mesh.

    Agitated with hydrate in glass bottle (closed) for 24 hours.

Ratio of Solution to Ore - 9.7 to 1 -weight basis.

Recovery based
on preg. sol.   <u>96.96% Pb</u>   <u>93.2% Zn</u>

NaOH Consumption
dry weight basis. 276 lb./ ton of ore.

Remarks: Head sample analysis not in agreement with
U.S. Bur.Mines Sta. Salt Lake. Writer used
care in rechecking his work and came to the
conclusion that sample received was not
entirely represenative of lot sampled by the
U. S. Bur.

          The excellent recovery gained in this test;
due to suggestions by Walter Palmer as to
filtering medium for tails; and knowledge
as to the correct strength hydrate to use.

'BIN' ORE TEST

	wt.	%Pb	%Zn	%Na$_2$CO$_3$	%NaOH
Head ore	100 g.	7.24%	32.40%	– –	– –
Hydrate sol. on	975.2 g.	.00	.00	2.33%	28.75%
Pregnant sol. off.	525. g.	.68%	2.75%	3.61%	24.51%
H$_2$0 wash.	550. g.	.00	.00	.00	.00
2nd. Preg. sol. off	972.2 g.	.29	1.24	3.92	11.84
Tail	55. g.	.88	10.78	– –	– –

Time of treatment   18 hours

NaOH consumption   490 lbs/ton of ore, 367 lb. NaOH/ton ore)
                                                    to Na$_2$CO$_3$ approx.)
Crushed to pass 20 mesh.

Recovery based on pregnant hydrate: 93% lead, 81.8% zinc

Remarks: The recovery in this test should have been
greater for the zinc. The advantage gained by a barren
wash with water was more than off set by the coarse condition
of the ore. The writer is of the opinion that at least
90% of the zinc could be extracted by grinding to - 100 mesh.

ORE TEST   (2nd lot from Symondson of Goodsprings, Nev.)

	Wt.	Vol.	%Pb	%Zn	Pheno.	Meth.red	
Head ore	100	--	2.98	24.60			
Sol. on	576	400	.00	.00	945	952	46.2%NaOH 1.3%Na_2CO_3 *
1st. sol. off preg.	834	632	.26	2.00	145	180	
water on (wash)	375	375	.00	.00	00	00	
2nd. preg. sol. off	533	485	.10	.83	--	--	
Tail	57		1.40	5.94	--	--	

Sample of ore stage pulverized to pass 100% -100 mesh.

Treatment time 24 hours

Recovery: based on first and second pregnant solutions.
86.3% of the Zinc   89% of the Lead

NaOH Consumption * impossible to calculate because of the water washes introduced in the test but not shown in the above table.

Effective strength of NaOH used in test. 28.75% NaOH

Remarks: The recovery of lead was almost perfect when due allowance is made for the lead sulfide present. The tails were examined and showed unaltered galena. For which mineral no claim is made that it is the least bit soluble in sodium hydrate.

Experiment To determine if $ZnCO_3$ ore is at all soluble in a Na_2CO_3 Sol by means of electrolysis.

Set up:

P. Diff between electrodes + 4. volts
Amp - No instruments.
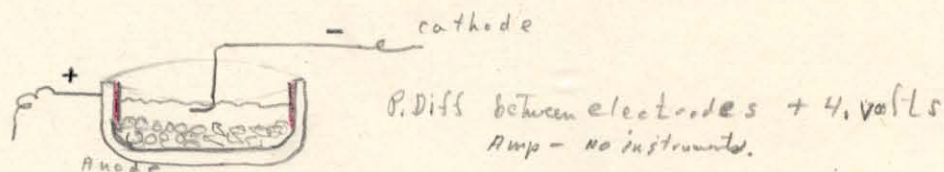
Cast Iron- anode made up from a iron pot coated with wax on the upper inner surface. Coated with wax to cause current to travel thru the ore and not directly between the Fe wire cathode & anode.

100 grams of ore thru 100 mesh — 2nd lot from Symondson; Good springs Nev.
500 cc $^{sol H_2O}$ of 10% by wt Na_2CO_3 (110.3 g Na_2CO_3/Liter) Net wt of 500cc = 551.5 grams
% Pb 2.98 % Zn 24.6 ore analysis.

Remarks.; Trace only of Pb deposited on the cathode; No Zinc.
The cathode gassed strongly Anode slight Hydrogen gas.
Added 10 grams NaCl — result Fe pot anode attacked by Cl_2 yielding $FeCl_2$ which + Na_2CO_3 → $Fe_2(CO_3)_3$ which floated to surface of Solution No doubt due to entrapped gases. $Fe_2(CO_3)$ is insoluble

Conclusions: (1) When the strength of a Sodium hydrate solution saturated with NaCl is allowed to become fouled with Na_2CO_3 and NaOH practically Nil; trouble can be expected if Fe anodes are used for electrolysis due to the Cl_2 liberated

(2) $ZnCO_3$ ores are not soluble in Soda ash solutions.

Experiment to determine it Zn ores are partially Sol in Low Strength NaOH can they be entirely recovered if the Sol portion of Zn is constantly removed to permit more Zn to enter the solution.

Set up:

- cathode Fe wire
+ Anode Fe pot
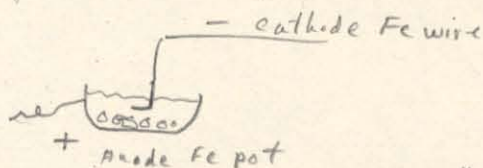
500 cc 10% NaOH aqueous solution + 5gr NaCl

100 grams ore   2.98 % Pb   24.6 % Zn   thru 100 mesh!

15 grams sponge Metal recovered at cathode after 48 hrs electrolysis

74 g Tail

Titration of Sol before & after electrolysis showed almost complete conversion of the NaOH to Na_2CO_3 during electrolysis

Conclusions: Any strength NaOH solution could be used to dissolve a $ZnCO_3$ ore providing there was a constant removal of the dissolved zinc and also provision either made to hold the Strength of the hydrate at a given level or provision made to convert the Na_2CO_3 formed back into NaOH by means of $Ca(OH)_2$

This experiment more or less futile in light of existing data available on the solubility of Pb and Zn in NaOH Solutions. In other words it could have been entirely forecasted what the results would be.
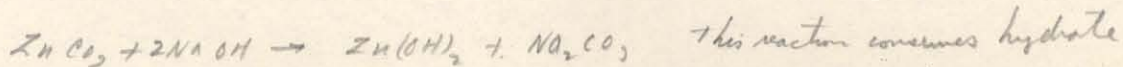
$$ZnCO_3 + 2NaOH \rightarrow Zn(OH)_2 + Na_2CO_3$$ this reaction consumes hydrate
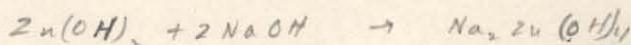
$$Zn(OH)_2 + 2NaOH \rightarrow Na_2Zn(OH)_4$$ this reaction richly represents what might be called a "mechanical" dissolution of Zn and does not consume hydrate in or under conditions of electrolysis

SOLUBILITY OF LEAD AND ZINC MINERALS IN SODIUM HYDRATE

Tables of lead and zinc minerals, arranged into groups according to their relative solubility in sodium hydrate, are on pages ___ to ___ of this report. The tables are divided into three main divisions for both lead and zinc minerals. The first division lists minerals soluble in sodium hydrate. The second division lists minerals of undertain or questionable solubility in sodium hydrate. The third division lists minerals of definite insolubility. In general the tables with a few exceptions contain only minerals found in Nevada_/.

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_/ Nevada's Common Minerals: Nev. Bur. Mines, vol. 35, no. 6, pp. 90 - 97, Sept. 1941.

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The term soluble is used only in a practical sense. The writer prefers to consider as soluble only those minerals that it would be practical to treat with sodium hydrate from metallurgical viewpoint. Prolonged treatment time, or complicated processes might result in the decomposition of some of the minerals listed as insoluble, however the profit motive would exclude such minerals from metallurgical consideration.

The tables are based upon data taken from the literature and experimental research by the writer. Artificial and natural sulfides of lead and zinc were carefully tested for possible solubility in aqueous solutions of sodium hydrate.

Prolonged agitation of solutions, application of heat to solutions, and extreme fine grinding were all tried. The hydrate solution was filtered off in each test and no trace of either lead or zinc found by the ordinary metallurgical schemes of analysis._/

_____

_/Low, A. H., Technical Methods of Ore Analysis: 1 st. ed.,1905.

_____

Upon the results of the foregoing tests, the writer decided to definitly place the sulfides of lead and zinc minerals among the insoluble group.

Experimental work on chemically prepared lead carbonate yielded some useful information. To one gram of $PbCO_3$, 20 grams of 50% sodium hydrate were added. Only a trace of the $PbCO_3$ dissolved. (This result could have be expected. See the PbO - NaO table, page   this report). A reaction however took place between the hydrate and the lead carbonate. The red oxide of lead (Pb_3O_4) was formed. To the mixture twenty cc'c of water were added, resulting in the equivalent of a 25% hydrate solution. The lead still refused to dissolve even with application of heat to the mixture. The writer decided to try a weaker hydrate solution, so to a second one gram portion of $PbCO_3$, forty grams of 25% hydrate were added. All of the lead carbonate immediately dissolved upon slight agitation of the solution.

The solution was evaporated by boiling. Lead hydroxide began to precipitate when the solution had been evaporated to about one-fifth of the original volume. Upon addition of water, after the mixture cooled, the lead hydroxide immediately went back into solution.

The foregoing experimental results illustrate why the mineral cerrussite ($PbCO_3$) was placed among the lead minerals soluble in hydrate. Some authors indicate the formula of the lead mineral minium as $2PbO.PbO_2$. This might lead to the deduction that minium is soluble in hydrate being made up in a sense of massicot (PbO) and plattnerite (PbO_2) soluble in hydrate_/.

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_/ Handbook of Chemistry and Physics, pg. 398, 26th. ed., Chemical Rubber Publishing Co., 1943.

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The formula for minium may also be written as Pb_3O_4 by simply re-writing or collecting together the Pb's and the O's in formula $2PbO.PbO_2$; some authors write it as Pb_3O_4. Experimental work indicates that Pb_3O_4 resists dissolution by hydrate solutions. Until the solubility of minium is definitly established it therefore is much more conservative to place under the questionable list.

The writer experimentally checked the solubilities of metallic lead and metallic zinc in hydrate solutions.

CONSUMPTION OF SODIUM HYDRATE

The pregnant hydrate solution removed from the residual pulp left after

Metallic lead and metallic zinc are both soluble in hydrate solutions. An interesting fact worth noting is their relative rates of dissolution. Metallic zinc dissolves with great rapidity, while metallic lead is relatively slowley attacked by sodium hydrate in aqueous solution. The converse seems to so in the case of lead and zinc carbonates. The lead carbonate dissolves faster than the zinc.

No satisfactory data concerning the solubility of the lead and zinc minerals in combination with iron or copper was found by the writer, hence they are listed under questionable solubility.

One may state as a general rule with few exceptions that the solubilities of the lead and zinc minerals conform to the following chemical combinations:

Soluble minerals	Insoluble minerals
arsenates	antimonides
antimonates	arsenides
carbonates	selenides
halides	sulphides
molybdates	sulpho - salts
phosphates	
silicates	
sulphates	
tungstates	
vanadates	

ZINC MINERALS AND COMPOUNDS SOLUBLE IN SODIUM HYDRATE

Adamite	$Zn_3As_2O_8Zn(OH)_2$
Calamine	$2ZnO.SiO_2H_2O$ or ZnH_2SiO_5
Fowlerite	$(Mn,Zn)O.SiO_2$
Gahnite	$ZnAl_2O_4$ or $ZnO.Al_2O_3$
Goslarite	$ZnSO_4.7H_2O$
Hemimorphite	$2ZnOSiO_2H_2O$
Hopeite	$3ZnOP_2O_5.4H_2O$
Hydroxide	$Zn(OH)_2$
Hydrozincite	$2ZnCO_33Zn(OH)_2$ or $ZnCO_3.2Zn(OH)_2$
Kottigite	$Zn_3(AsO_4)_2.8H_2O$
Monheimite	$(Zn,Fe)CO_3$
Smithsonite	$ZnCO_3$
Troostite	$Zn_2(Mn)_2SiO_4$
Willemite	$Zn_2SiO_4 + Mn$
Zinc	Zn metallic
Zincite	ZnO
Zinkosite	$ZnSO_4$

ZINC MINERALS OF QUESTIONABLE SOLUBILITY IN SODIUM HYDRATE

Aurichalcite	$2(Zn,Cu)CO_3.3(Zn,Cu)(OH)_2$
Descloizite	$2(Pb,Zn,Cu)O.V_2O_4(OH)_2$
Franklinite	$(Fe,Zn,Mn)(FeO_2)_2$ or $ZnO.Fe_2O_3$
Fluosilicate	$ZnSiF_6.6H_2O$
Tennantite	$Cu_3SbS_3x(Fe,Zn)_6As_2S_9$

ZINC MINERALS INSOLUBLE IN SODIUM HYDRATE

Ferrite	$ZnFe_2O_3$
Marmatite	$(Zn,Fe)S$
Sphalerite	ZnS
Tetrahedrite	$5Cu_2S.2(Cu,Fe,Zn)S.2Sb_2S_3$
Wurzite	ZnS

LEAD MINERALS SOLUBLE IN SODIUM HYDRATE

Alamosite	$PbSiO_3$
Anglesite	$PbSO_4$
Belmontite	A lead silicate
Beudantite	$2PbO.3Fe_2O_3.2SO_3\ As_2O_5.6H_2O$
Bindheimite	A hydrous antimonate of Pb
Cerrussite	$PbCO_3$
Cotunnite	$PbCl_2$
Crocoite	$PbCrO_4$
Cromfordite	$PbCl_2.PbCO_3$
Ecdemite	$Pb_4As_2O_7 2PbCl_2$
Hydrocerrussite	$2PbCO_3.Pb(OH)_2$
Lanarkite	$Pb_2O(SO_4)$ or $PbSO_4 PbO$
Laurionite	$PbCl_2 Pb(OH)_2$
Lead	Metallic
Leadhillite	$Pb(OH)_2 PbSO_4.2PbCO_3$
Lead Oxide	PbO
Litharge	PbO
Lithargite	PbO
Massicot-	PbO
Matlockite	$PbO.PbCl_2$
Mendipite	$2PbO.PbCl_2$

LEAD MINERALS SOLUBLE IN SODIUM HYDRATE - Continued

Mimetite. . . . . $9PbO.3As_2O_5.PbCl_2$

or

$(PbCl)Pb_4(AsO_4)_3$

Paralaurionite. . . . . $PbCl_2Pb(OH)_2$

Penfieldite . . . . $PbO.2PbCl_2$

Phosgenite . . . . $PbCl_2.PbCO_3$

Plattnerite . . . . PbO_2

Pyromorphite . . . . $PbCl_2.3Pb_3(PO_4)_2$

or

$(PbCl)Pb_4(PO_4)_3$

or

$Pb_5P_3O_{12}Cl$

Raspite . . . . $PbOWO_3$ or $PbWO_4$

Stolzite . . . . $PbOWO_3$ or $PbWO_4$

Vanadinite . . . . $(PbCl)Pb_4(VO_4)_3$

or

$9PbO.3V_2O_5.PbCl_2$

Wulfenite . . . . $PbMoO_4$

LEAD MINERALS OF QUESTIONABLE SOLUBILITY IN SODIUM HYDRATE

Beaverite $CuO.PbO.Fe_2O_3.2SO_34H_2O$

Caledonite $2(Pb,Cu)O.SO_3H_2O$

Descloizite $2(Pb,Cu)O.V_2O_4(OH)_2$

Ganomalite $4CaO.6PbO.6SiO_2.H_2O$

Linarite	$(Pb,Cu)SO_4 \cdot (Pb,Cu)(OH)_2$
Minium	$2PbO.PbO_2$ or Pb_3O_4
Mottramite	$2(Pb,Cu)O.V_2O_4(OH)_2$
Percylite	$PbCl_2.CuO.H_2O$
Plumbojarosite	$PbFe_6(OH)_{12}(SO_4)_4$ or $PbO.3Fe_2O_3 \; 4SO_3.6H_2O$

LEAD MINERALS INSOLUBLE IN SODIUM HYDRATE

Andorite	$2PbS.AgS3Sb_2S_3$
Benjaminite	$(Cu,Ag)_2S.2PbS.2Bi_2S_3$
Boulangerite	$5PbS.2Sb_2S_3$
Bournonite	$2PbS.Cu_2S.Sb_2S_3$ or $PbCuSbS_3$
Clausthalite	$PbSe$
Dufrenosite	$2PbS.As_2S_3$
Freieslebenite	$2Ag_2S.3PbS.2Sb_2S_3$
Galena	PbS
Jamesonite	$2PbS.Sb_2S_3$ or $Pb_2Sb_2S_5$
Meneghinite	$4PbS.Sb_2S_3$
Naumanite	Ag_2PbSe

REGENRATION OF HYDRATE SOLUTIONS WITH LIME

Sodium carbonate accumulates in the hydrate solutions directly proportional to the amounts of lead and zinc present as carbonates in an ore undergoing treatment. The sodium carbonate has no beneficial action as a solvent upon the lead and zinc present in an ore. _/

_ _

_/

_ _

The addition of lime (CaO) to regenerate the sodium hydroxide from hydrate solutions, fouled with sodium carbonate, is possible. The reaction proceeds as follows:

$$CaO + H_2O + Na_2CO_3 = 2NaOH + CaCO_3$$
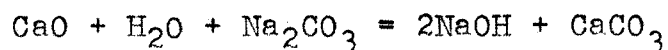
1 lb. of CaO will yield 1.4+ lbs. of NaOH

The above reaction works out satisfactorily, but trouble can be expected when lead and zinc salts are present in a fouled solution. Experiments were made on pregnant hydrate solution as follows: First lime was agitated in water, allowed to settle, then the soluble calcium hydroxide filtered off. This clear filtered solution of lime water was added to a hydrate solution containing 1.4% Zn, 1.7% Pb 0.9% Na_2CO_3 and 26% NaOH. An immediate precipitate formed, which was filted off and washed with water. This precipitate was

qualitatively tested for lead and zinc, with positive results for both metals. Exactly what chemical reaction occurs was not determined. The writer believes that the reaction is probably as follows:

$$Na_2Zn(OH)_4 + Ca(OH)_2 = 2NaOH + 2H_2O + CaZnO_2$$

This reaction proposed by the writer parallels one in the chemistry of precious metal cyanidation. The double cyanide salt, $K_2Zn(CN)_4$ or $Na_2Zn(CN)_4$, reacts with $Ca(OH)_2$ this way:

$$Na_2Zn(CN)_4 + 2Ca(OH)_2 = 2NaCN + Ca(CN)_2 + 2H_2O + CaZnO_2$$

The successful regeneration of the sodium cyanide salt depends on the insolubility of the calcium zincate formed. The irreversibility of the reaction depends on the calcium zincate being precipitated.

The writer did not feel that it was within the scope of this investigation to experiment with the effects of calcium hydroxide. There is considerable technical literature available written about the subject of the solubility of calcium salts. The explanations given are not entirely satisfactory. The writer did however make a careful study of the proposition to regenerate NaOH from hydrate solutions barren in lead and zinc. It is entirely feasable to regenerate hydrate solutions if the lead and or zinc has been previously removed by electrolysis or chemical means. Care should be used not to introduce an

excess of lime above that required to react with the Na_2CO_3. It will then be safe to use the hydrate over again to treat lead and zinc ores. Since a written discussion of the reasons for the writer's last statements would be too long for this report reference is given to the following:

Solubility of calcium hydroxide in water. (Haslam, Calingaert, and Taylor, 1924.); (Bassett, 1934); (Shenstone and Cundall, 1883.); (Grieve, Gurd and Mass, 1933.); (Larocque and Maass, 1935.)

Solubility of calcium hydroxide in aqueous salt solutions. (Cabot, 1897.); (Johnston, and Grove, 1931.);

Solubility of calcium hydroxide in aqueous solutions of salts. (Maigret, 1905.)

Solubility of calcium hydroxide in aqueous solutions of sodium hydroxide. (d'Anselme - Bull. soc. chim. (3), 29, 938, '03.);

Calcium hydroxide and alkali carbonates and hydroxides. (Bodlander - Z. angew. Chem. 18, 1138, 1905.)

Calcium carbonate in aqueous solutions of salts. (Cameron and Robinson, 1907.); (Wells, 1918.); (Askew, 1923.)

Calcium carbonate in aqueous solutions of sodium carbonate. (Pratolongo. 1924.); (Bury and Redd, 1933.)

Calcium carbonate in aqueous solutions of sodium hydroxide. (LeBlanc and Novotny, 1906.); (Wegscheider and Walter, 1907)

SODIUM CARBONATE

$Na_2CO_3 \cdot 10H_2O$.
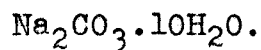
Solubility in Water
(Wells and McAdam, Jr., 1907; Mulder, below 27° and above 44°.)

t°.	Gms. Na_2CO_3 per 100 Gms. H_2O.	Solid Phase	t°.	Gms. Na_2CO_3 per 100 Gms. H_2O	Solid Phase
0	7.	$Na_2CO_3 \cdot 10H_2O$	34.76	48.98	$Na_2CO_3 \cdot 7H_2O$
5	9.5	"	35.62	50.08	"
10	12.5	"	35.50	...	" + $Na_2CO_3 \cdot H_2O$
15	16.4	"	29.86	50.53	$Na_2CO_3 \cdot H_2O$
20	21.5	"	31.80	50.31	"
27.84	34.20	"	35.17	49.63	"
29.33	37.40	"	36.45	49.36	"
30.35	40.12	"	37.91	49.11	"
31.45	43.25	"	41.94	48.51	"
32.06	45.64	"	43.94	47.98	"
32.15	...	" + $Na_2CO_3 10H_2O$	60	46.4	"
33.10	...	" + $Na_2CO_3 \cdot H_2O$	80	45.8	"
30.35	43.50	$Na_2CO_3 \cdot 7H_2O$	100	45.5	"
32.86	46.28	"	105	45.2	"

ZINC SILICATE DETERMINATION

To determine the amount of zinc silicate in a mixture of silicate and sulphide ores the following method was proposed by Buskett_/:

_/Buskett, Evans W., Simple methods of the assaying of zinc silicate: Mining and Engineering World, pg.255, Feb.,1913.

To one gram of the ore add 10 cc's of 50% acetic acid. Boil 10 minutes and filter. Wash with hot water. To the filtrate add 10 cc's of hydrochloric acid and 1 or 2 cc's of bromine water. Boil until the bromine is expelled. Dilute with cold water, add from 3 to 7 gms. of ammonium chloride, 10 cc's of stronger ammonia and boil. Filter and wash with hot water. It will not be necessary to redissolve the iron and there is generally very little of it. Neutralize with hydrochloric acid, add 10 cc's excess, dilute to 300 cc's. heat to boiling and titrate with a standard solution of potassium ferrocyanide.

EQUILIBRIUM IN THE SYSTEM SODIUM OXIDE, ZINC OXIDE AND WATER

AT 30°

(Goudriaan, 1919, 1920.)

Gms. per 100 gms. sat. sol.			Gms. per 100 gms. sat. sol.		
Na_2O	ZnO	Solid Phase	Na_2O	ZnO	Solid Phase
11.8	2.6	ZnO	39.4	9.0	$Na_2O.3H_2O$
17.4	5.0	"	39.6	7.2	"
23.7	11.3	"	40.7	2.0	"
27.3	16.0	"	40.5	1.6	"
27.8	16.5	" + $Na_2O.ZnO.4H_2O$	40.9	1.1	"
28.0	14.9	"	41.9	0.0	"
30.1	13.2	"	24.6	12.5	ZnO
31.8	11.7	"	19.9	15.2	$Zn(OH)_2$
33.2	11.2	"	13.7	7.2	"
34.7	10.4	"	10.1	4.7	"
36.1	10.2	"	4.6	1.0	"
39.2	9.7	" + $Na_2O.3H_2O$	4.5	0.4	ZnO

THE TREATMENT OF LEAD AND ZINC CARBONATE ORES

WITH SODIUM HYDRATE

Strong Hydrate on finely pulverized ores caused ore
to ball up and enclose a part in such a manner that the ore was
wetted by the solution.

Outline.

Percolation with no agitation is / out because ores tend to shrink in size to form a hard crust on the outer surfaces that becomes impermeable to hydrate.

Introduction.

~~~~ source of cheap NaOH

Costss

1
Chemical proceedures analytical - short method for sols.

2 Chemistry of the process
        zincate etc. equations
        NaCO$_3$ experiment

choice of electrodes. ? (Pt) *Zn Fe Cu* ← ok ← ok ← ok

out

H overvoltage too low

33

pg 1343 Ch. Hdbk;

Solubility product Zn(OH)$_2$ 1.8×10^{-14} $18° - 20°$

Zn S 1.2×10^{-23} PbSO$_4$ 1.06×10^{-8}

Pb CO$_3$ 3.3×10^{-14} Pb S 3.4×10^{-28}

Dissociation Constant Pb(OH)$_2$ Const for 2nd OH
                                             3×10^{-8}

Zn(OH)$_2$ 1.5×10^{-9}

INTRODUCTION

Numerous hydrometallurgical schemes have been proposed, utilizing a wide range of solvents for the extraction of lead and zinc from their ores.//

_/ Mellor vol. IV 1923

Present practice is however largly confined to the treatment of calcined zinc ores with sulfuric acid leaching. The direct treatment of Nevada Lead-Zinc carbonate ores with acid is not feasable, because ǿǿ the carbonates consume large amounts of acid. Roasting with subsequent acid leaching is not desirable because of the lack of cheap fuel in Nevada. The sulfide content or the carbonate ores is practically nil, therefore it would be necessary to introduce acid as a reagent.

Sodium hydrate offers an interesting solution to the problem especially in because this hydrate will be produced in connection with the magnesium industry at Las Vegas, Nev. The carbonates of lead and zincǿ are soluble in alkali (sodium hydrate_6/

_/ Physic & chem hnd bk pg.

This report deals primarily with the treatment of
carbonate   was   the
zinc/ores. The main reason for this ið because/samples of ore ~~f~~ availble for testing were from ~~the~~ Goodsprings Nev and found to be in general higher in zinc content then lead.

Zinc ~~minerals~~ carbonites ~~seemed~~ present more ~~trouble in~~ problems in dissolution than Lead, so more stress was placed on zinc extraction.

Should "costs" be brought in here?

2-2354
Ch.Ab.
The action of H_2S on alkaline solutions of Zn salts
L.W. McCay J. Amer. Chem. Soc. 30, 376-8 (Mar.)
Zn pptd. as ZnS from alkaline Solutions is soluble in an excess
of H_2S.

P7-3000
Ch.Ab.
Ger. 259,234. July 16, 1910, E. Flugger. Production of
ZnO and ZnS from Zn lyes by removing the foreign metals & subse
quently ppt. the Zn as oxide,hydroxide or sulfide C.f. Ch.Ab 6-2982

6-2982
Brit., 11,103, May 8, 1911. E. Flugger Zinc oxide ~~Anthl/thl~~
and sulfide from the pure zincate, ZnO is obtained by pptn.
with H_2O above 80° or by heating to 100° in vacuo the hydrated
ppt obtained at lower temperatures, while ZnS is obtained by
pptg the soln. with H_2S or other sol sulfides and lithopone
by pptg. with BaS in the presence of H_2SO_4 or a sol. sulfate
by mixing the sulfide ppt. with $BaSO_4$

c.f. Ch.Ab. 6-2299

6-2299
C.A.
Ger. 243,653, Feb. 3, 1910 Ed Flugger
Scrap Zinc charged into a closed vessel with a solution of 1 H_2O to
2 NaOH (98%) the amt of NaOH soln. used is such that the chaarge is
covered and the product contains 1/2 the NaOH combined as Zincate.
heat to b for about 3 hrs. the resulting zincate sol is drawn off
mixed with three times the amt of H_2O already present, in order to
separate the impurities. To ppt. the Zn, the clear filtrate
is poured into 5 times the amt of hot H_2O, ZnO sepg. out quickly
and clearly, and being dried to pure white powder. The remaining
liquor is evapd. and used for the soln of fresh amts of Zn.

A Dictionary of Chem Solubilities Comey & Hattn 1921 pg. 1126

ZnS soluble in NaClO in Alkaline sol.
Reference (Sadtler, Trans.Am. Electorchem. Soc.
1902, 1. 142

18- 2842 C.A. The electrolysis of Ammoniacal Zn Carbonate Sols.
T.P. Campbell Trans Am Electro chem. Soc.
46 preprint 1924

RELATIONSHIP BETWEEN % NaOH and Normality

%	G/liter	Normality
1	1o.1	.252
2	20.41	.51
3	30.95	.773
4	41.71	1.042
5	52.69	1.315
6	63.89	1.596
7	75.31	1.879
8	86.95	2.17
9	98.81	2.463
10	110.9	2.765
12	135.7	
14	161.4	
16	188.	
18	215.5	
20	243.8	6.08
22	273.0	
24	303.1	
26	334.0	
28	365.8	
30	398.4	9.96
32	431.7	
34	465.7	
36	500.4	
38	535.8	13.38
40	572.0	14.29
42	608.7	
44	646.1	
46	684.2	
48	723.1	
50	762.7	19.06

The system Zinc Oxide - sodium Oxide - water

R. Scholder & G. Hendrich. Zeitschrift für anorganische und
allgemeine Chem. 241, 76 - 92 (1939) Avail at Univ Cal at Los Ang
Univ.Utah. Slt.Lk., Cal Tech Pasadena, Univ of Cal.Berkley

The isotherms at 20° and 100° for the system $ZnO-Na_2O-H_2O$ in a
conc. range 1 - 21 N NaOH were determined. as were the isotherms
at 30° and 40° for the conc. range 13 to 20 N NaOH.
At 20° the stable solid phases are (1) ZnO between 0 and 13.4 N NaOH,
(2) $(Zn(OH)_3)Na$ between 13.5 and 19.6 N,   (3) $(Zn(OH)_4)Na_2$
between 19.7 & 20.1 N,   (4) a mixture of $(Zn(OH)_4)Na_2$ and $NaOH.H_2O$
beyond 20.1 N. The soly of ZnO rises, while that of the monosodium
zincate decreases wit increasing NaOH conc. causing a shappe
break in the curve at 13.5 N NaOH

Metastable solid phases with higher solubilities found at 20° were
 (1) ZnOH $Zn(OH)_2$ rhombic,up to 7.2 N NaOH and (2) $(Zn(OH)_3)Na.3H_2O$
between 7.3 and 13.3 N NaOH. The soly of this second metastable
solid shows a min. in 10 N NaOH.

At 100° the stable solid phases are ZnO and $(Zn(OH)_3)Na$, the
latter appearing above a conc. of 19 N NaOH. The sol of ZnO
 changes only slightly with temperature,being less at 100°

The isotherms at 30° &40° were detd. for $(Zn(OH)_3)Na$
The soly. of this salt increases with rising temperature for
equal conc. of NaOH

Chem Ab. 117.7 - (1939) for dope on filtering Alkali sol in the
laboratory if wanted.

EQUILIBRIUM IN THE SYSTEM SODIUM OXIDE, ZINC OXIDE AND WATER

AT 30°

(Goudriaan, 1919, 1920.)

Gms. per 100 gms. sat. sol. Na$_2$O	ZnO		Solid Phase	Gms. per 100 gms. sat. sol. Na$_2$O		ZnO	Solid Phase
11.8	2.6	2.07	ZnO	39.4		9.0	Na$_2$O.3H$_2$O
17.4	5.0	4.02	"	39.6		7.2	"
23.7	11.3	9.1	"	40.7		2.0	"
27.3	16.0	12.9	"	40.5		1.6	"
27.8	16.5	13.3	" + Na$_2$O.ZnO.4H$_2$O	40.9		1.1	"
28.0	14.9	12	"	41.9		0.0	"
30.1	13.2	10.6	"	24.6		12.5	ZnO
31.8	11.7		"	25.8 19.9	18.6	15.2	Zn(OH)$_2$
33.2	11.2		"	17.75 13.7	8.8	7.2	"
34.7	10.4		"	13.1 10.1	5.75	4.7	"
36.1	10.2		"	5.96 4.6	1.22	1.0	"
39.2	9.7		" + Na$_2$O.3H$_2$O	5.83 4.5	.49	0.4	ZnO

Ger., 217,632, Oct. 6, 1908 Edoardo Sanna, Iglesias, Sardinia.
Utilizing Electrolytic Zinc Sponge by washing it in a $NaNO_3$ sol.,
warming it while still wet moist to 100° - 150°, and at the same
time subjecting it to a pressure of about 1000 kg/sq.cm., whereby
the Zn sponge is converted into a dense, metallic Zn, ready for
market.
P 4:1432[1] Chem Abstracts

Brit., 24,631, Oct. 26, 1909 E. Sanna (same data as above)
Italy P5:345 Chem. Ab.

Ger., 282,234, June 29, 1913. Chem Fabrik Griesheim - Elektron
Rendering Electrolytic Zn Sponge Permanent.
Electrolyte removed by H_2O wash. Sol. if strongly alkaline pass
in CO_2 gas because Na_2CO_3 more readily washed out than alkali.
Low temperature and vacume employed with stirring
Zn Sponge of 90% -99% Zn content
Permanent in air and exceeds Zn dust in activity.

2:383[4] P 9:2193[7] Chem Ab.
Ch Ab. Titration of Zinc in Alkaline Solution   To the filtrate after
digestion with NH_4Cl and NH_4OH, heat to boiling, titrate with
$K_4Fe(CN)_6$ Use $FeCl_3$ in HAc (add a few drops $FeCl_3$ to glacial HAc)
as an indicator.

7:765[8] Brit., 21,014, Sep 22, 1911. C.V. Thierry.
Ch.Ab. In the recovery of Zn from "blue powder" the powder is washed
with acid in order to remove the oxide coating from the particles
The powder shaken up with H_2O and the required amt. of acid,
preferably HCl is added. The sol of $ZnCl_2$ is decanted, and may
be/recovered conc. to recover the salt, and the powder after
washing is compressed to a block and may be fused.

P-8:2337[9] NH_3 on Calamine Cao used to regenerate $NH_4)_2CO_3$ A $ZnNH_3$
Ch.Ab. lye has very little coef. of friction and filter readilly
without use of pressure.

P-8-1563[1] Ger. 267,531 April 12, 1912. E.A.Ashcroft   Separating metals
Ch. Ab. from zinciferous metals ores or other materials, whereby salts of
the contained metals are obtained in solution and the metals
present are pptd. as hydroxides by NH_4OH.

7-1337 Determination of Zn Silicate in the presence of ZnS
 Ch. Ab.
7-1338 See also statement solubility of $ZnSiO_4$ in NH_4OH.

10-1130 J.H. Hildebrand and W.G. Bowers J. Am. Chem. Soc. 38-785-8 (1916)
Ch.Ab. Usual textbook explanation
$$H_2ZnO_2 + 2OH^- = 2H_2O + ZnO_2^{--} \text{ not correct}$$

$$H_2ZnO_2 + OH^- = H_2O + HZnO_2^- \text{ correct}$$

Excellent reference to the technical phases of Zn chemistry (RLM)
Part of the alkali is adsorbed, changing the coagulum of $Zn(OH)_2$
to a suspension and part neutralizes the hydroxide, giving the
acid zincate.

Na₂O₂ZnO 4H₂O + Na₂O 3H₂O

Na₂O 3H₂O

ZnO + Na₂O2ZnO 4H₂O

Na₂O ZnO 4H₂O

ZnO

ZnO +

ZnO

ZnO

Zn(OH)₂

Zn(OH)₂

ZnO

ZnO

Na_2O

Zinc as ZnO

Flow sheet

Bins
↓
Crusher
↓
Mill
↓
Agitators

ΣK 1st check

Filter
TAIL
Sludge

→ write + show Nernst equation
why this is practical

Zn Dust

PPt. Pb   Sponge

Filter   To   Press + melt

Pure (NaZn) Sol   Electrolytic cells

Filter

Sludge

? ?

TO TAILS
conc. to
recover
Pb + Zn Sulfide

NaOH
Feed TANK

+   -   ?

Sump

CaO Slurry
tank

CaCO_3
↓
TAIL

Cathode
Zn
deposit
↓
Press + meltes

Return barren
sol

A barren H$_2$O wash of the tails not desirable except to recover sodium carbonate.

The percolation of ores not desirable because of the formation of a crust.

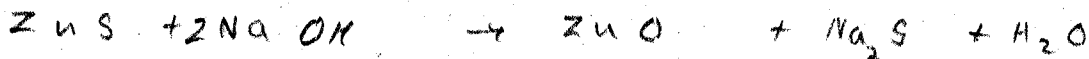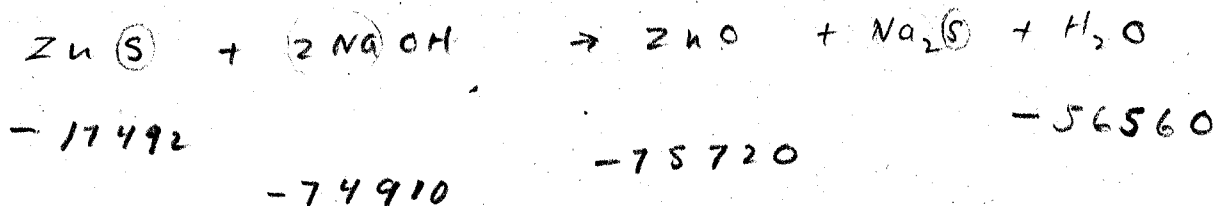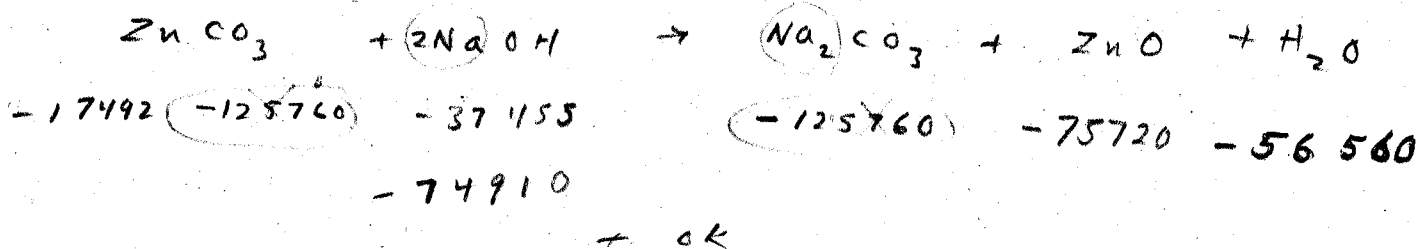A iron pot offers a way to tell amt of Na OH required with great rapidity.

Na$_2$CO$_3$ slow no dissolution

Na$_2$CO$_3$ has no dissolution effects on ZnCO$_3$ tried & proven electrolytically in test F-III

$ZnS + 2NaOH \rightarrow ZnO + Na_2S + H_2O$

S   23 450   ~~2×62588 Na~~   ~~37455~~   Na 2 - 62 588
Zn   - 17 492   2×37455   S   23 450
         S

   23 450   OH   - 75 720   ~~2)62588~~
  -17 492   - 74 910   +23450
  + 5958   5958   -56 560
           - 68 952
           ± 23 450
           - 92 402   ΔF +

$ZnCO_3 + 2NaOH \rightarrow Na_2CO_3 + ZnO + H_2O$

-17492 (-125760)   - 37 455   (-125760)   -75720   -56 560
        -74910
              ok

$Zn \circledS + 2NaOH \rightarrow ZnO + Na_2 \circledS + H_2O$

  - 17492   -56560
        -74910   -75720

                      Fe_2O_3

$2Fe + \frac{3}{2}O_2$ 3904
  0

$\frac{1}{3} + \frac{1}{4}$ mult. $\frac{1}{2} \times \frac{1}{4} = \frac{1}{8}$ $\frac{1}{2} + \frac{1}{4}$ $\frac{\frac{2}{1}}{\frac{1}{4}} \frac{3}{4}$

    a = 10   div $\frac{1}{2} \div \frac{1}{4} = 2$ $a^3 b^6 c^2 \div a^2 b^2$

   a+b = 16

     b = ? a $a b^4 c^2$ $\frac{1}{3} - \frac{1}{4}$

            $\sqrt{144}$ $\frac{4}{12}$

$\sqrt{562839}$

       13   (12)   12.1   12.0 $\frac{3}{12} \frac{1}{12}$

    526   782   733

December 9, 1942

Mr. H. C. Lee   J. R. Bradford & L. F. Bayer

USE OF CAUSTIC SODA SOLUTIONS OR CELL LIQUOR FOR
TREATMENT OF ORES

Purpose

At the present time there is no economic market for the large amount of caustic soda which will be produced here by the chlorine plant due to the high freight rate on caustic soda to an established market of sufficient size to consume this production. Therefore, it has been proposed to use the cell liquor from the chlorine plant or the caustic soda produced from the cell liquor for treating ores in this district for the recovery of metal from them.

Summary

Preliminary leaching tests using either caustic soda or cell liquor have been made on oxidized Pb-Zn ores from the Goodsprings district. These tests have shown that good extractions, 95% of the Pb and 90% of the Zn, can be made when using either about a 30% NaOH solution or cell liquor. Also preliminary tests indicate that satisfactory metal products can be made from the metal in these solutions by precipitating the metals from the solutions electrolytically. Other ores which may lend themselves to treatment with caustic soda are as follows: Manganese, Tungsten, Molybdenum, Vanadium, Cobalt, etc.

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Procedure

The tests were made by fine grinding the ore and then leaching portions of it with a caustic soda solution or chlorine plant cell liquor with various conditions. The following conditions were varied until a combination was found which gave best results: (1) strength of solution, (2) amount of solution, (3) temperature of solution, (4) treatment time and (5) fineness of ore.

The tests were made by leaching in a beaker and using a mechanical stirrer during the leaching period. After the leaching was completed the pulp was filtered on a Buchner filter. The filter cake was washed, dried and analyzed. The filtrate was sampled and analyzed, and the remainder saved for making tests to determine the best method of precipitating the dissolved metals from these solutions. Electrolytic precipitation and precipitation with CO_2 were tried. Only a crude set-up was available for the electrolytic precipitation, which consisted of a car storage battery and an ammeter. Therefore, the results are only indicative of what might be done.

Results

The results of the tests show the following:

(1) An extraction of 91.8% of the Zn and 94.2% of the Pb from the ore can be obtained by leaching for one hour at 220°F. with a 25% NaOH solution. Test No. 26.

(2) An extraction of 91.2% of the Zn and 96.9% of the Pb from the ore can be obtained by leaching for two hours at 220°F. with a solution containing 20% NaOH and 10% NaCl. Test No. 17.

(3) An extraction of 92.1% of the Zn and 97.5% of the Pb from the ore can be obtained by leaching for 2½ hours at 220°F. with chlorine plant cell liquor containing 150.8 grams per liter NaOH and 153.7 grams per liter NaCl. Test No. 16.

(4) Tests indicate that the Pb and Zn in the leach solutions may be separated electrolytically by precipitating the Pb first at a lower voltage than used for the Zn. A test using a 6-volt storage batteryas a source of power and regulating the voltage by the number of cells used, gave the following analysis. Test No. 37.

	Pb	Zn
Pb product	92.2%	3.31%
Zn "	9.4%	81.86%

(5) The Pb and Zn in the leach solutions can be precipitated by carbonating the solutions. The results of the tests indicate that the separation of the Pb and Zn by this method is not as good as obtained by electrolytic separation.

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Conclusions and Recommendations

Since preliminary tests only on oxidized Pb-Zn ore from the Goodsprings district have been made, no conclusion can be reached on the general suggestion of using the caustic soda from the chlorine plant for extracting the metal from the ores in this locality.

The ore from the Goodsprings district was tested first because these ores have been extensively developed and are close by as well as representing a substantial tonnage. Other ores of this type should also be tested before making any extensive tests on the Goodsprings ore.

The use of a solution containing both NaOH and NaCl for leaching ores appears to be a new idea and may be patentable. If there is any possibility of using such a process, it may be advisable to take out a patent for protection.

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OFFICE OF WAR INFORMATION

Department of the Interior

For Release _____

Important discoveries of high-grade zinc and lead ores—two critical and essential war materials—have been made by Bureau of Mines engineers through test drilling at the Yellow Pine mine property in the Goodsprings district of Clark County in southeastern Nevada, it was announced by Secretary of the Interior Harold L. Ickes.

One block of ore is estimated to contain 35,000 tons of high-grade zinc ore and individual samples from some of the numerous test-holes drilled in the area have assayed as high as 46 percent zinc and 57 percent lead, according to information submitted to Secretary Ickes by Dr. R. R. Sayers, Director of the Bureau of Mines. One of the samples showed two percent copper in addition to the other metals.

"Preliminary diamond drilling and sampling indicates favorable prospects for developing new and important ore bodies containing zinc and lead to assist the Nation in alleviating a critical situation with regard to zinc," Dr. Sayers informed the Secretary.

One of the more recent undertakings in the Bureau's extensive war minerals exploratory program, the Goodsprings project was started in September, 1942—less than four months ago—and the results have been gratifying in view of the fact that the engineers have been working such a short time, Dr. Sayers said.

"Unfortunately, funds allotted for this particular project have been exhausted and no further funds are available for transfer within the Bureau of Mines," the Director advised Secretary Ickes. "Therefore, it was necessary to stop work on this project the second week in January."

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Determination of the approximate tonnage and grade of all the reserve lead and zinc ores in the district will depend upon additional drilling and analyses of samples, the Director explained in pointing out the desirability of completing the investigation of what may turn out to be a major mineral discovery.

In describing the exploratory work in the Goodsprings district, which is southwest of Las Vegas and near the Nevada-California state line, Bureau engineers reported that the ore discoveries were adjacent to old workings which were thought near depletion, as well as in entirely new areas.

Working far underground in the Yellow Pine mine, the Bureau's crews drilled a hole upward from the 800-foot level and out into ore assaying 17.6 percent lead and 10.4 percent zinc. A similar hole from the 900-foot level was in ore for a distance of 26 feet and it averaged 24.1 percent zinc and 11.7 percent lead. Other drill holes on the 800-foot level revealed a probable continuation of one of the larger deposits of ore.

Diamond drilling on the surface near the Yellow Pine workings revealed a body of ore more than 1,000 feet long, from 25 to 50 feet wide, and ranging in thickness from 2 to 26 feet, the engineers reported. This is the block that is estimated to contain 55,000 tons of ore assaying 22.2 percent zinc. Geological conditions indicate that its length may extend more than half a mile. However, additional drilling will be necessary to prove the continuity of the deposit.

Summarizing the Goodsprings exploratory work to date, Director Sayers said that assays of samples from the explored zones averaged 21.29 percent zinc and 9.55 percent lead, while individual samples ran as high as 46 percent zinc and 37 percent lead.

"Production in the Goodsprings area could be stimulated by exploratory work on other properties in this vicinity," Dr. Sayers stated. Some of the properties which show promise are Potosi, Milford No. 1, Milford No. 2, Sultan, Root Hill, Whale, Argentina, Carbonate King Zinc Mine, Anchor and Hoosier.

MINING AND GEOLOGY OF THE GOODSPRINGS DISTRICT

The mines of the Goodsprings district are scattered over an area 18 miles long
and 7 miles wide, 25 miles southwest of Las Vegas in the Spring Mountains.
The northern and higher extension forms the prominent range west of Las Vegas.
A few mines, such as the Yellow Pine in the center of the district, are
readily accessible by road, but many are locate on cliffy slopes high
in the mountains and must be reached by tortuous trails and the ore lowered to
the base of the mountains by aerial trams.

Mining began in the district in 1856 but the production remained small until
the turn of the century. It reached it's peak during the decade from 1910 to
1920. About one fourth of the 74 mines have accounted for 95% of the production.
In the past two years only 14 of the mines have opperated and most of the
production hs come from 6 mines, namely the Anchor, Argentena, Green Monster,
Root, Sultan, and Yellow Pine. The gross yield of the district from the 90s
to the present is in excess of $10,000,000, half of which is to be credited to
the Yellow Pine mine.

The ore deposits of the district include those which have been exploited
for gold, silver, copper, cobalt, molybdenum, vanadium, platinum, palladium,
lad, and zinc. The quantity and value of the lead-zinc ores for exceeds
those of the other metals. During 1943 and the first half of 1944, about
An ave. of about
30,000 tons of ore containing 28% zinc and 2.5% 4.0 lead were sold to the Metals
shipped from the district
Reserve Company stockpile at Jean, seven miles east of Goodsprings.

In the lead-zinc mines very little timber is required. Some of the
larger stopes have been mines by benching from the top of the stopes; some
by using square sets purely as a means of extracting the ore and not as
supports for the backs. Generally the square sets were removed after extraction
of the ore and used over again. In the Potosi mine rock walls and fill were
used in the bottoms of the stopes as an aid in extracting the ore from the backs.

Only a very few stopes were timbered to support the country rock. These stopes
are in areas where the stopes were in contact with porphyry which weathers
rapidly and sluffs off; locally timber has been required where the stopes
are against the Bird Spring sandstone which tends to slab off. Generally
speaking, despite the intensity of faulting and the general broken nature of
the ground, the country rock stands indefinitely with no timber.

The zinc- lead ratio of the ores is variable. A few lead mines contain little
or no zinc and a few zinc mines little or no lead, but considering the district
as a whole, the zinc-lead ratio averages between 3 and 4 to 1.

The mineralogy is generally quite simple. The zinc sulphide in all but
a few deposits is almost completely oxidized to the silicate Calamine, and
to the carbonates hydrozincite and smithsonite. Galena, the lead sulphide,
is quite common but is locally oxidized to the sulphate anglesite, and to the
carbonate Cerussite.

The stratified rocks exposed in the area attain a thickness of 13,000
feet and range in age from Cambrian to Recent. All systems of the Paleozioc
are represented in the 8,500 feet of beds exposed. Of the Paleozoics, limestone
and dolomite make up more than 7,000 feet. All of the lead-zinc deposits are
in paleozoic beds older than the Permian and the vast majority lie within a 500
foot zone of Mississippian strata.

The Mesozoic section attains a thickness of over 4,000 feet and is, made
up largely of sandstone, shale, and conglomerate, with some limestone at the
base. The prominent red and tan sandstone cliffs southwest of Las Vegas
belong to this system.

The Tertiary is represented by tuffs and lava flows.
Although
to the casual observer the structure appears simple, the region reveals an
amazing record of folding, thrust faulting, and normal faulting. At some
time between the late Jurassic and middle Tertiary, the beds were folded to
different degrees depending on the massiveness of the bedding. Toward the

end of the epoch of ~~thrust~~ folding thrust faults began to form. The Goodsprings
area displays 4 major and many minor thrusts, which generally dip west. Near
the end of the epoch of thrusting, sills and dikes of granite porphyry were
intruded. After the thrusting a few normal faults developed which were
later mineralized. These faults were followed by other normal faults which
are younger than the ore deposits but older than the middle tertiary lavas.

The ore deposits are limestone replacements which generally parallel the
bedding. Some are tabular but many are irregular in outline. Most occur
where fractures have broken the more massive beds. Thrust faults parallel
or nearly parallel to the bedding locally brecciated the rock. Sulphide
solutions rising on the high angle faults encountered the breccia zones,
spred out in them and replaced the breccia and to a certain extent the
unbroken wall rock. Later these deposits were oxidized with little migration
taking place during or after oxidation as is evidenced by the usual occurence
of sulphide relicts, ~~usually~~ commonly galena, ~~but sphalerite has also been found in~~
~~several of the mines.~~ Small bodies of white hydrozincite have been found below some
of the larger ore bodies and are believed to have been formed by downward mi
migration of part of the zinc during oxidation. These bodies of white hydrozincite,
however, are relatively small and few in number.

The most common impurities in the ore are limonite and unreplaced ribs
and blocks of dolomite. Locally, as at the Argentena mine, barite is a
common gangue mineral.

At what depth the sulphide zone will be encountered is not known from
data on hand and will probably not be known until exploration extends to
much greater depths than has been attained in any of the mines. The present
distribution of zinc sulphide offers no clues. The highest mine in the
district, the Potosi, contains the largest amount of zinc sulphide, some of which
is within 200 feet of the surface.

Of the mines which ahve operated in recent years the Yellow Pine,
Anchor, and Argentena, have ben selected for brief discussion.

The Yellow Pine is the largest and deepest mine in the district with
27,000 feet of workings on 12 levels reaching a depth of 600 feet.

The Yellow Pine has produced 50,000 tons of zinc and 50,000 tons of
lead. Most of the production was during the 20,years from 1906 to 1928.

The mine workings explore three members of the Missippian Monte Cristo
limestone. The oldest, the Bullion member, is here a massive gray dolomite.
Overlying the Bullion is the Arrowhead which consists of 10 feet of limestone
and dolomite in units a few inches thick separated by thin seams of black
shale. Above the Arrowhead is the Yellow Pine member, here consisting of
about 100 feet of thinkbedded limestone and dolomite. Although the ore
deposits of the mine lie in these three members, the Yellow Pine member has
been by far the most productive horizon. The Yellow Pine is un-conformably
overlain by the Bird Spring formationwhich here has 50 feet of sandstone
at it's base. The sedimentary rocks are cut by dikes and sills of granite
porphyry. The largest porphyry body is a sill with its base along the
top of the basal Bird Spring sandstone.

In general the Yellow Pine mine reflects the general structure of the
Goodsprings district on a small scale. The sediments strike northest and dip
northwest at an average of 40°. They are broken by thrusts which likewise
dip west but ate flatter than the bedding. Displacement on individual
thrusts is small and amounts to only a few scéore of feet.
Brecciation along the thrusts varies in amount from place to pbce. Locally
the shearing may be distributed through a zone 20 feet thick and elsewhere the
shears cut cleanly through the rock with little or no breccia being present.
Although the evidence is inconclusive, the larger masses of breccia appear
to be at places where bedding shears and steeper thrusts branch from the main

thrusts.

The thrusts are displaced by two systems of moderately to steeply dipping f
faults along which the movement is believed to have been mostly horizontal.
The older of these two systems includes faults trending between northwest
and west-northwest; the younger, or Alice system, includes arcuate faults which
generally trend north. The displacement is usually but a fe feet although
faults with displacements of as much as 250 feet are present. Both sets
are believed to be premineral as indicated by the occurrence of galena
in fissures which can be assigned to one or the other of the two systems.
Galena is most common along faults of the Alice system. As a consequence
of an early stage of thrusting and two stages of high angle faulting, the
ground is generally briken throughout.

The Yellow Pine ore bodies are typically tabular with the longest dimension
paralleling the strike of the bedding.

Past records indicate that the zinc content of the crude ores has varied from
5 to 45%. No doubt the primary ore bodies were predominantly sphalerite and
galena. Subsequent to its deposition the ore has been oxidized to some
unknown depth below the deepest workings in the mine.

Judging by the ore now showing in the mine, the typical ore is a friable
agregate of calamine crystals intergrown with small hydrozincite crystals
or is massive pink hydrozincite.
and coated with limonitic material. Between the richer stringers of ore
barren ribs of dolomite which may be as much as 10 feet thick but which
in the richer zones average less than one foot and comprise less than 20%
of the material extracted.

The Anchor mine, 5 miles south of Goodsprings, is high in a rugged canyon in the Spring Mountains. The ore is transferred from the mine to the base of the mountain by a 2,000 foot aerial tram. A 200 foot inclined shaft leads to the 3 principal levels of the mine.

Since 1908 the production has been over 4,000 tons of zinc and 3,000 tons of lead. Some of the ore mined during the last war contained as high as 40% zinc but during the past few years the ore shipped 20% zinc and a few percent lead. During the past two years the Anchor has been the largest producer in the district.

The ore bodies lie in the Anchor member of the Monte Cristo limestone. This member underlies the Bullion member which is the eldest lowest stratigraphic unit encountered in the Yellow Pine workings. The Anchor member is largely a dolomite in the vicinity of the mine. Lenticular pods of chert locally make up from one third to one half of the beds. A 25 foot cherty unit in the Anchor with from 3 to 4 feet of very cherty beds at the top and bottom, is the key horizon in the mine. All of the ore has been mined from this general zone and from the immediately overlying beds.

A series of low angle thrusts cut the mine workings. Some thrusts are essentially bedding slips but others are steeper or flatter than the bedding. There are gentle flexures in the bedding both along the strike and down the dip. The thrusts are believed to have originated as bedding slips which broke into thrusts at flexures in the bedding. Brecciation is generally greater in the cherty units and is possibly due to the chert lentils acting as pegs in the bedding planes, preventing simple slipping.

The top of the hanging wall stope over the main ore body and the lower end of the main ore body were in lead ore containing little zinc. The chief ore mineral for the mine as a whole, however, is largely pink hydrozincite.

Pre and post mineral normal faults are present. Most of these strike roughly parallel to the bedding. Those dipping west are believed to be

premineral and a few of these were probably feeders. Those dipping east are post mineral. The largest known displacement on any of these faults is 20 feet.

Near the lower end of the main ore body, two west dipping faults have unsheared galena along them. The ore in the vicinity of the westernmost of these two faults contained mostly lead but up dip from the eastern fault zinc was the most important metal mined.

The Argentena mine is 2.5 miles southwest of Goodsprings near the crest of the Spring Mountains. As at he Anchor, the ore is lowered to the base of the mountains by an aerial tram but unlike the Anchor, the mine can be reached by road.

The overall total production from the Argentena is much less than many mines in the district but in recent years it has been one of the leading producers of lead-zinc ores. Most of the developement work has been done on the property since 1928. Approximately 12,000 tons of ore have been shipped, about one one fourth of which contained 38% combined lead and zinc and the remainder including the recent production about 23% combined metals. The zinc-lead ratio varies from 3.6 to 1 to 7 to 1.

The ore bodies at the Argentena lie entirely within the Yellow Pine dolomite and are largely concentrated in the upper 30 feet of the formation. In the Argentena area dips of over 10° are not common.

The mine workings and surrounding area are cut by a strong anastomosing series of north-south trending tear faults in the hanging wall of the Keystone thrust. That The movement on these faults was almost horizontal . These faults are believed to be premineral although locally it would appear that there has been some post mineral movement as well. Underground these breccia zonesshow many closely spaced shears along many of which the dolomite is ground to a flour. In contrast to other mines discussed, the breccia of these

strong zones rarely contains ore, although the minor faults between the major breaks are locally highly mineralized. In contrast to the rocks along the major breaks, these minor fractures are more open and apparently furnished easier passage for the ore solutions than the major fault zones.

Thrusts are relatively unimportant and few in number in the Argentena workings. The ore tends to make to a large degree along the bedding but also makes along the high angle faults.

The ore is largely calamine with irregular pods of smithsonite and hydrozincite. Locally an earthy vanadate, probably descloizite is abundant.

As at the Yellow Pine and Anchor mines the ore contains ribs and boulders of dolomite. The ore in some of the workings contains a considerable amount of barite. Locally the barite is so abundant that the ore can not be profitably mined bt present hand sorting methods.

Since almost all mining in the district is done by leasors, and much of that by local residents with limited capital, little attempt is made to block out ore and known reserves at any one time are small. In the mines which I have seen, there is only a relatively small amount of high grade oe in sight. Locally the low gade reserves are much larger but do not add up to any great tonnage. With few exceptions the ore bodies that have been explored in the district were exposed by erosion.

The ore controls for the district as a whole, and even for the mines here discussed are as yet theories that have not been conclusively proven. The problem is a difficult one but in time, by setting up theories based upon actual observation, and by constant reevaluation of these theories as more and more deposits are examined, it is hoped that the ore controls can be worked out a and can be applied to areas away from the present workings as well as to ground adjacent to them.

Considering that the 74 mines and numerous prospects are scattered over a district containing more than 100 square miles, the job of detailed study is an enormous one. However, when one considers the shallowness of exploration to date, it is only reasonabe to assume that there must be many times the tonnage of past production remaining to be found in the area.