

A METHOD  
FOR THE  
PRODUCTION OF BARIUM HYDROXIDE  
FROM  
BARYTES

Thesis

by

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for the degree of Bachelor of Science  
in Chemical Engineering

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Aim

The aim of this investigation has been to select a process for the commercial production of Barium hydroxide from barytes, and to determine the most favorable conditions for its operation.

Abstract of Results

The inertness of barytes has led to many experiments and patents for its reduction. It was decided to effect the reduction of the barytes in a cement kiln with carbon. The temperature of the greatest yield with the least water insoluble material is between 1000°C and 1100°C and with a minimum period of heating. The yield is about 87% of the original barytes. The resulting BaS is quenched with water and ground to 20 mesh. The leaching is very quickly accomplished and the temperature of the solution is raised 80°C to bring more material into solution. The solution is then filtered, a theoretical amount of CuO added and the mixture boiled. The resulting CuS is filtered off and CuO regenerated by roasting. The Ba(OH)<sub>2</sub> solution is evaporated down and the solid precipitated out by cooling. The material is in the form of

$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , and must be heated to a dark red heat to drive off all the water of crystallization.

### History and Importance

Barytes is a natural sulfate of barium.

It usually appears associated with silica, lime and iron, and is a very cheap source of barium compounds, costing but \$5--\$10 per ton at the mine and \$26 per ton when floated and purified. Extensive deposits are found in Missouri and the southern Appalachian states and in England.

The problem of reducing the barytes to the sulfide has been the subject of much investigation since about 1910 as  $\text{BaS}$  and  $\text{BaO}$  were formerly used for desaccharizing molasses as  $\text{CaO}$  is used in the Steffens process today.  $\text{CaO}$  has recently superseded  $\text{BaS}$  and  $\text{BaO}$  due to its lower cost and almost equal desaccharizing action.

It was formerly thought that a solution of  $\text{BaS}$  if sufficiently cooled, would precipitate  $\text{Ba}(\text{OH})_2$  crystals. This theory was proven erroneous by Terres and Erüçkner<sup>1</sup> who showed that a double salt  $\text{Ba}(\text{SH})(\text{OH})5\text{H}_2\text{O}$  separated out when

<sup>1</sup> Z.E. 26 1--20 (1920)

A list of abbreviations used in this report is given on page 20

a BaS solution was cooled. Thus a correct method of obtaining  $\text{Ba}(\text{OH})_2$  from BaS must be investigated.

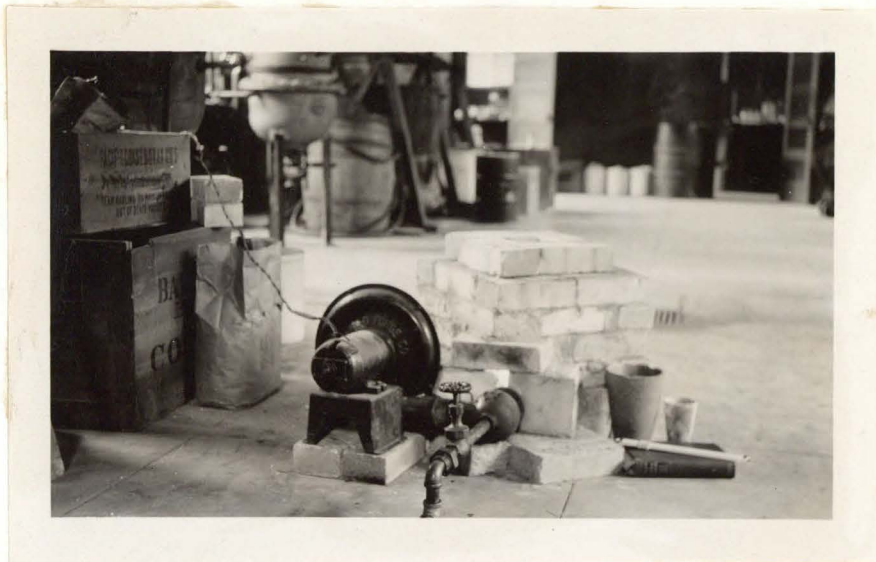
### Materials

The barytes used was the same as used by paint manufacturers and averaged 91% pure, with no iron or silica. The charcoal for the reduction of the barytes was finely powdered as this was found to greatly increase the yield of BaS.

### Apparatus

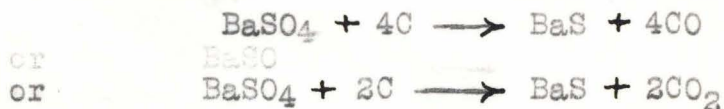
As the first part of the experimental investigation (that of reducing the barytes to BaS) was well covered in the literature, it was thought best to concentrate effort on the second part, (that of converting BaS into  $\text{Ba}(\text{OH})_2$ ). No BaS was found available so it was necessary to prepare some, not for the purpose of obtaining the greatest yield but merely to afford material to work on. For this purpose a small scale furnace was designed to handle about a three pound charge. It was constructed of fire brick bound together by high temperature cement. Gas was used to fire the furnace and a special type of burner equipped with an electric fan blower was needed to attain the  $1000^\circ\text{C}$  needed for the reduction of the Barytes. The furnace was made just large enough to accomo-

date one size L fire clay crucible.



### Theory

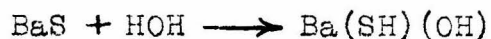
The reduction of the barytes may be accomplished in either of two ways.



From the investigations of A.E. Wells ' it is probable that the former equation more nearly represents the facts of the case and that a reaction following the first equation gives considerably better yields than one following the second. Upon dissolving the BaS in water a reaction takes place according to the following

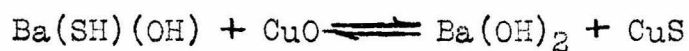
' J.I.E.C. 8, 776 (1916)

equation,



as was established by Terres and Brückner <sup>1</sup>.

The formation of this double salt and the separation out of the same upon cooling the solution made it impossible to obtain  $\text{Ba}(\text{OH})_2$  by this method. As suggested by Darcet and Vogel (described by Terres and Brückner) the sulfur can be removed from the solution by boiling with finely divided  $\text{CuO}$ .



The  $\text{CuO}$  is regenerated merely by heating the  $\text{CuS}$  above  $220^\circ\text{C}$  in contact with air.



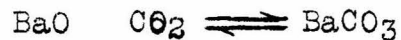
### Procedure

As mentioned before the literature on the subject of the reduction of barytes to the sulfide is voluminous and much time was spent on going over it. It was thought wise to keep a file of the articles on analysis of barium compounds as well as those on the reaction itself. The bibliography follows.

<sup>1</sup> Z.E. 26 1--24 (1920)

M. Herzberg C.A. 2 1867 (1908)

BaO<sub>2</sub> prevents the reaction



from going to the right.

C.E. Jacobs C.A. 2 2716 (1908)

A charge of BaCO<sub>3</sub> 40 parts and coking coal 16 parts, finely powdered produces BaO of exceptionally porous structure.

C. Rollin C.A. 6 1969 (1912)

BaO may be produced by heating Ba(OH)<sub>2</sub> in a furnace on the floor of which is Ba(NO<sub>3</sub>)<sub>2</sub>.

G.A. Barbieri C.A. 7 2019 (1913)

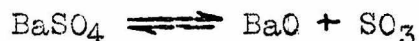
A charge of BaSO<sub>4</sub>, 100 kilograms, Carbon 28 kilograms, and Na<sub>2</sub>SO<sub>4</sub> 7 kilograms, heated in an electric furnace yielded BaS, 90.3%, BaO 3.8%, Ba<sub>2</sub>C 2.6%, and Na<sub>2</sub>S 1.8%. The water insoluble material amounted to only 1.5%.

Chem. Fab. Cosweg (P) C.A. 7 2670 (1913)

BaCO<sub>3</sub> heated under reduced pressure yields a very high percentage of exceptionally porous BaO.

L.E. Saunders C.A. 8 3841 (1914)

In an electric arc furnace lined with BaSO<sub>4</sub> without the use of carbon, 75% of the BaSO<sub>4</sub> was converted into BaO.



S.B. Newberry and H.N. Barrett C.A. 9 1374 (1915)

By mixing BaSO<sub>4</sub> and BaO in equal proportions and pulverizing till 90% passes thru 100 mesh and heating and agitating the same at 1460°C a high quality and good yield of BaO is obtained. SO<sub>2</sub> and O<sub>2</sub> are evolved in the process. The BaO prevents the charge from fusing together.

R. De Forerand C.A. 3 623 (1909)

Ba(OH)<sub>2</sub> 8H<sub>2</sub>O is heated in a stream of H<sub>2</sub> and BaO is obtained if the temperature is kept above 600°C. This article also gives the thermo-chemistry of the oxide. (Abstracted from A.C.P. 15 (8) 433-90 (1908))

C.B. C.A. 6 2652 (1912)

BaS is highly poisonous. A fatal dose of BaCl<sub>2</sub> is 10-15 gms. An investigation of poisoning by barium salts.

Chr. A. Beringer C.A. 6 3170 (1912)

Soluble barium compounds may be pre-



pared by igniting a mixture of  $\text{BaSO}_4$  and an alumina and silica containing substance at bright red heat. The barium-aluminum-silicate thus formed is decomposable by acid.

H.O. Hofman and W. Wanjokow C.A. 7 30 (1913)

Abstracted from the B.A.I.M.E. 69 889-943. Curves are plotted showing the dissociation and decomposition temperatures of alkali earth metals when heated in a current of dry air.

W. Mosttowitsch C.A. 5 841 (1911)

Pure  $\text{BaSO}_4$  heated for 15-30 minutes in dry air remains unchanged up to  $1400^\circ\text{C}$ . First dissociation is noticeable at  $1500^\circ\text{C}$ . At  $1580^\circ\text{C}$  it melts. Decomposition of  $\text{BaSO}_4$  by  $\text{SiO}_2$  begins at  $1000^\circ\text{C}$  and forms silicates.  $\text{FeO}$  decomposes  $\text{BaSO}_4$  at  $1000^\circ\text{C}$ . Reduction of  $\text{BaSO}_4$  by carbon begins at  $600^\circ\text{C}$  and is complete by  $800^\circ\text{C}$ .  $\text{CO}$  begins to reduce  $\text{BaSO}_4$  at  $650^\circ\text{C}$  and completes the reduction by  $800^\circ\text{C}$ .  $\text{BaS}$  remains unchanged at  $1000^\circ\text{C}$ . It loses some of its sulfur at  $1200^\circ\text{C}$ .

J.F. Sacher C.A. 7 1465 (1913)

Analysis of  $\text{BaS}$  by precipitation with an excess of  $\text{Pb}(\text{NO}_3)_2$  and back titrating the

$\text{Pb}(\text{NO}_3)_2$  with  $(\text{NH}_4)_2\text{MoO}_4$ .

G. von Staszewski C. A. 9 358 (1915)

BaS is obtained by heating  $\text{BaSO}_4$  in a rotary furnace in the presence of hot furnace gases passing thru the furnace in the same direction as the charge. The temperature is maintained at  $900^\circ\text{C}$ . The CO is burnt and returned to the furnace,

I.L. Marino C.A. 7 3202 (1913)

Abstracted from G.C.I. 43-416. An electric rotary furnace is described which makes use of water gas and illuminating gas for the reduction of  $\text{BaSO}_4$  at  $525^\circ\text{C}$ . The gas enters at the exit end and a yield of 95-98% is claimed.

W.E. Prisk and H.R. Harrison C.A. 12 982 (1918)

BaS is purified by filtering its solution thru successive layers of  $\text{MnO}_2$  and granulated  $\text{CaCO}_3$ .

J. Waddell C.A. 12 1445 (1918)

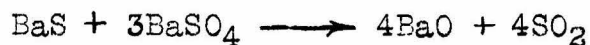
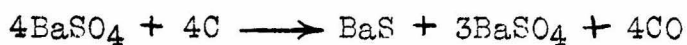
Barium can be volumetrically determined by means of  $\text{BaCrO}_4$  and KI. (Also see C.A. 14 2314, 14 3613 for similar methods).

G.M. Adhikari et. al. C.A. 17 1535 (1923)

Details and precautions for reducing  
BaSO<sub>4</sub> are set forth.

U. 2 177

BaSO<sub>4</sub> is reduced with coke and the  
resulting BaS is heated in an electric fur-  
nace with more BaSO<sub>4</sub> to obtain the oxide.



Abstracted from J.C.I. 21-391 (1902)

W. 1 442 (Old Ed.)

Add BaS to hot water, filter and add  
CuO or ZnO to decompose the BaS. Evaporate  
the material to dryness and heat to red heat  
to obtain Ba(OH)<sub>2</sub>. Heating Ba(OH)<sub>2</sub> in a  
stream of air produces BaO and H<sub>2</sub>O. BaO is  
also formed by heating BaSO<sub>4</sub> in the presence  
of steam. (See P. 55-415.)

T. 1 546 (New Ed.)

BaS is prepared by heating 100 parts  
of BaSO<sub>4</sub> with 20 parts of coal slack or  
charcoal. An admixture of resin oil or  
sawdust is advantageous as is asphalt from  
gas works for hydrogen containing products

prevent the formation of polysulfides.

The addition of common salt aids fusion of the  $\text{BaSO}_4$ . A charge of the following composition heated in a reverberatory furnace gave good results; 100 parts  $\text{BaSO}_4$ , 200 parts  $\text{NaCl}$ , and 15 parts of charcoal.

The analytical methods for determining sulfur found were:

- (1) Determination with  $\text{PbAc}_2$ --After Treadwell.
- (2) Determination by oxidizing S to  $\text{SO}_4$  by means of  $\text{H}_2\text{O}_2$ .
- (3) Volumetric determination by titration with  $\text{HCl}$  using phenolphthalein and methyl orange as indicators.
- (4) Volumetric determination using Iodine.
  - (a) This method is not very accurate due to the loss of  $\text{H}_2\text{S}$  from the diluted solution.

It is very easily seen that the problem resolves itself into two minor problems, the first that of reducing the barytes to the sulfide and the subsequent conversion of the sulfide to the hydroxide.

Preliminary Work

Some trouble was experienced in analyzing the barytes. It was thought best to follow the method of Toch <sup>1</sup>, who advises fusing one gram of the sample with five grams of anhydrous  $\text{Na}_2\text{CO}_3$ . This was carried out in a porcelain crucible. After fusing the sample was leached, until it disintegrated, with 100 c.c. of water and then filtered. The residue of  $\text{BaCO}_3$  was washed and 25 c.c. of  $\text{HCl}$  (1:3) added. After boiling to remove the  $\text{CO}_2$  and neutralizing with  $\text{NH}_4\text{OH}$  and then making slightly acid with  $\text{HNO}_3$ , dilute  $\text{H}_2\text{SO}_4$  was added to precipitate the barium. The  $\text{BaSO}_4$  was then determined in a Gooch crucible. As the high heat (from a blast lamp) cracked one crucible and the two other determinations gave discordant results, (differing 17%) it was decided to use a nickel crucible. Lead in the sample was determined as it has a damaging effect on both nickel and platinum and amounted to less than 0.05%. Results with the nickel

<sup>1</sup> Chemistry and Technology of Paints P 314

varied 5%. Using a platinum crucible the sample was found to contain 91%  $\text{BaSO}_4$  with determination varying less than 1%. No iron or silica was found present, the 9% being probably  $\text{BaCO}_3$ . As this has no effect on the process further analyzing was thought unwarranted.

The barytes was reduced in the furnace described. A mix of 10 pounds of barytes and 1.56 pounds of powdered charcoal (after proportions of Wells) sufficed for three charges, which were heated at  $1000^\circ\text{C}$  for one hour and forty-five minutes. The yield was about 60%.

### Experimental

Some of the  $\text{BaS}$  was dried and run thru the pulverizer. It was found that the heat generated in the pulverizing oxidized about 50% of the  $\text{BaS}$  back to  $\text{BaSO}_4$ . Inasmuch as the  $\text{BaS}$  is quenched in water (or  $\text{Ba}(\text{OH})_2$  solution from the final crystallization) it is more convenient to pulverize wet.

As previously stated,  $\text{Ba}(\text{SH})(\text{OH})5\text{H}_2\text{O}$  crystals separate from the solution of  $\text{BaS}$  when cooled. Two methods of obtaining  $\text{Ba}(\text{OH})_2$  were suggested.

(1) By changing the S compounds with metallic

oxides as CuO or ZnO which give insoluble sulfides as first advanced by Darcet and Vogel.

(2) By driving out H<sub>2</sub>S by passing CO<sub>2</sub> thru a hot saturated solution whereby barium precipitates as BaCO<sub>3</sub> and is changed to BaO by heating.

Tests made by Terres and Brückner showed that desulfurization with CuO is complete and reacts in molecular proportions. This method was chosen for the desulfurization of the Ba(SH)(OH) because it was simpler and had no difficultly handled gases in the reactions. On titrating, the solution prepared in the laboratory with HCl using first phenolphthalein and then Methyl orange as indicators to obtain the OH and SH concentrations respectively, it was found that they occurred in exactly equal quantities.

The first experiment consisted in boiling 10 c.c. of solution and .329 gms. CuO (finely powdered) for 20 minutes. The solution was then filtered and titrated. It was found to contain less than 1.5% SH.

200 c.c. of solution was treated in a similar way, the time required being 20 minutes. Here less than 2.5% SH remained.

Another 200 c.c. sample was treated in the

above manner and the filtrate evaporated almost to dryness. The  $\text{Ba}(\text{OH})_2$  obtained was very pure and contained less than .24% SH.

Experiments with the leaching of the BaS showed that it took place very rapidly thus indicating that the process would not be held up appreciably for the leaching operation.

There was quite a tendency for  $\text{BaCO}_3$  to form on the surface of the barium solutions while working with them. However in commercial apparatus the access of air would not be so free and this trouble would not be so bothersome.

It is important to note the effect of iron on the reduction of barytes. Comparative tests made by Wells gave the following results:

Material	Percent of Total Barium in Compounds (Average of 4 tests.)		
	Water Soluble	Acid Soluble	Acid Insoluble
Pure $\text{BaSO}_4$	80	10	10
$\text{BaSO}_4$ with 6% Fe	68	17	15

This indicates that the presence of iron in the Barytes reduces the amount of BaS formed materially. Consequently this impurity is to be avoided if possible.



Conclusions

It is quite apparent that the desulfurization of  $\text{Ba}(\text{SH})(\text{OH})$  can be accomplished on a commercial scale by  $\text{CuO}$ . It now remains to choose the method of reducing the barytes to the sulfide. Many electric arc and electric furnace processes are prominent in the literature and are apparently successful. However the high cost of electrical power especially in this part of the country practically prohibits the use of these processes. The very thorough investigation of the reduction of barytes by A.E. Wells ' gives many possibilities. Probably the most practical method investigated was that using a cement kiln. This was 12 feet long and 10 inches inside diameter. The number of revolutions was 1.15 per minute. The hot gases enter at the exit end. The temperature is maintained at  $1050^{\circ}\text{C}$ . The ratio of pulverized coke to barytes is .15 and the rate of charge is 19.1 pounds per hour. The gas consumption is 5.6 cubic feet per minute. With these conditions a yield of 87% water-soluble barium compounds was obtained.

' J.I.E.C. 8 776 (1916)

Recommendations

The barytes and coke mixed in proper proportions can be pulverized in a small Hardinge Mill.

The cement kiln type of furnace seems to be suited very well to the reduction reaction.

The stack gases coming from the furnace at about 450°C can be used to roast the CuS in a muffle furnace to regenerate CuO for the desulfurization reaction.

The quenched BaS should be pulverized wet in a Hardinge Mill and then leached in a system of tanks employing parallel flow of H<sub>2</sub>O (or Ba(OH)<sub>2</sub>) and the BaS. This may be accomplished by means of connecting vats into which the discharge of BaS is rotated. The solution should be at about 80°C for best leaching conditions.

The CuO and BaS solution are introduced into a reaction chamber and are agitated by means of air and the mixture heated for 30 minutes by indirect steam.

A filtration is now necessary to obtain the purest Ba(OH)<sub>2</sub> and probably a rotary filter would be best for this kind of precipitate.

The solution is then taken down almost to dryness in a salting out evaporator, the crystals being centrifuged to remove excess solution. They are then washed and dried by means of a tunnel drier of a controlled humidity type.

#### Suggestions Regarding Supplementary Investigation

The interesting problem remains of changing the  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  to  $\text{Ba}(\text{OH})_2$ . According to O. Bauer the change from  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  to  $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  is effected by boiling the solution of  $\text{Ba}(\text{OH})_2$ . By melting crystals of  $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  at  $100^\circ\text{C}$  they are converted into  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ . By heating the latter at dark red heat  $\text{Ba}(\text{OH})_2$  is obtained. To obtain  $\text{BaO}$  it is necessary to heat  $\text{Ba}(\text{OH})_2$  to a clear white heat. These reactions and a method for carrying them out should prove an interesting commercial problem.

The economic aspect of the problem should offer a fruitful field of research. As mentioned before commercial Barytes is offered on the market in two forms, i.e., just as it comes from the mines, and the floated and purified Barytes.

The cost of the ore at the mine is from \$5 to \$10 per ton according to the purity, while the floated material costs around \$26 per ton. If the material as it comes from the mines does not contain an excessive amount of detrimental iron it is very possible that this form would be used, thus reducing the cost of materials greatly. If too much iron were found present it might be possible to give the ore a simple preliminary treatment to render it available for the process.

Baryte Ore (at mine)	\$8 per ton	\$.004 per pound
Floated Barytes		.0118 per pound
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O		.045 per pound
Coke Breeze	\$6 per ton	.003 per pound

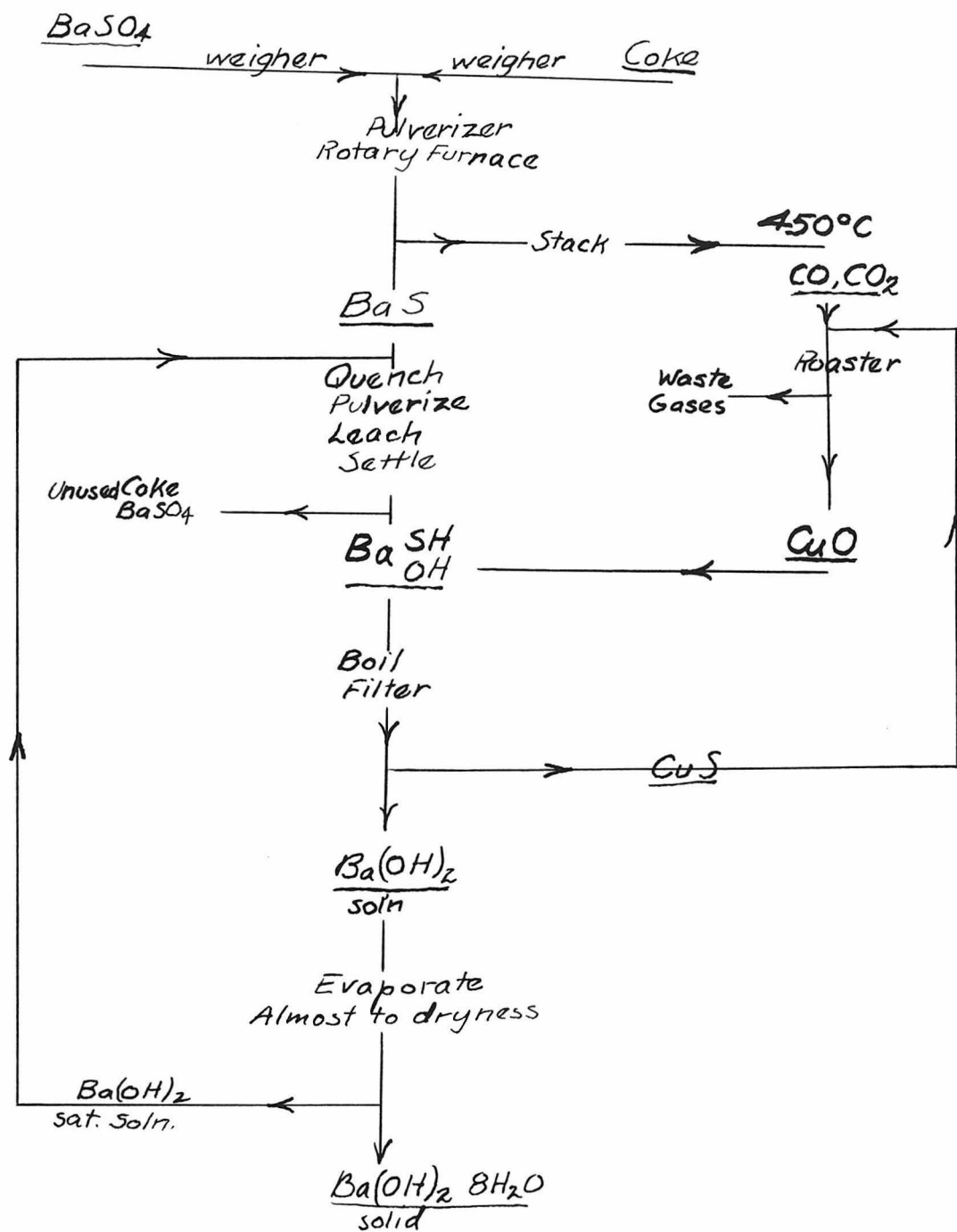
Using the ore as it comes from the mine the cost of materials would be only \$.0038 per pound of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O produced, whereas the market price of the product is \$.045 per pound.

#### Acknowledgement

The author wishes to express his whole-hearted thanks and appreciation for the timely advice and counsel of Dr. Wm.N. Lacey and for the opportunity of having been able to work with and under the guidance of him in this piece of research.

Abbreviations

- C.A.--Chemical Abstracts
- Z.--Zentralblatt
- U.--Ullman's encyclopedia of Technical Chemistry
- J.C.I.--Journal of the Chemical Industry
- W.--Watts' Dictionary
- P.--Poggendorffs Annalen der Physik und Chemie.
- T.--Thorpe's Dictionary
- Z.E.p--Zeitschrift für Electrochemie
- J.I.E.C.--Journal of Industrial & Eng. Chemistry
- B.A.I.M.E.--Bulletin of the Amer. Inst. of Mining  
Eng.
- G.C.I.--Gazzetta Chimie Italiana
- Z.A.C.--Zeitschrift für Anorganische Chemie



Flow Sheet



# SOLUBILITY CURVES

of  
 $Ba(OH)_2$  and  $BaS$   
after  
Terres and Brückner

