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THE ROASTING OF PITCHBLEND E ORE

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THE ROASTING OF PITCHBLEND ORE

By O. J. Buckheim, H. C. Kloepper, R. M. Paine,
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Introduction

The sulfur content of recent lots of pitchblende has been ranging up to 10% sulfur. This amount of sulfur consumes considerable quantities of nitric acid and barium carbonate. It was thought that roasting of the ore before digestion might remove a substantial portion of the sulfur and thereby effect economics in the use of nitric acid and barium carbonate over the added cost of roasting. The present study includes the effect of air and steam roasting on the sulfur content, uranium recovery, acid consumption, and filtration rate of several ores, including those of both high and low initial sulfur content.

Conclusions

1. Increasing the temperature of the air roast increases both the sulfur removal and the filtration rate, but also increases the uranium loss in the leached digest cake.
2. The length of time of roast has a much smaller effect than the temperature on sulfur removal and filtration rate.
3. A steam roast removes as much sulfur as an air roast; it does not increase the filtration rate; it increases the uranium losses in the leached digest residue to a lesser extent.
4. Increased air flow and thinner beds lead to increased sulfur removal.
5. Acid leaching of the digest cake will reduce the uranium loss to about half the loss by a carbonate leaching.
6. The uranium losses after either the acid leach or the carbonate leach of the digest cake from the roasted ores are too high to be tolerated.

Equipment

The Tube Furnace

The burnout experiments were run in a tube furnace which was equipped with a quartz tube about 1-1/4 in. in diameter. The ends were fitted with rubber stoppers containing the inlet and exit gas tubes. The inlet stopper also contained a chromal-alumel thermocouple in a stainless steel thermowell. By regulating the current supplied to the furnace by means of a Powerstat, the temperature could be controlled to within $\pm 10^\circ \text{C}$ within the hot zone of the furnace.

The air supplied to the furnace was metered by measuring the pressure difference across an orifice. The orifice was calibrated by passing air through the orifice, through two Milligan bubblers in series and then through a Precision Hot Test Meter, and timing the flow through the meter. The bubblers were put in the line during calibration as they created considerable back pressure. The volume of air was measured at atmospheric pressure, however, and the

orifice was so calibrated. Due to variations in line pressure, timing etc., the calibration is probably accurate to $\pm 5\%$.

The overall accuracy of the tube furnace set up was about $\pm 1\%$ as evidenced by duplicate and triplicate runs on the same material.

Steam from the steam roasting of ores was provided by an electrically heated steam generator. This generator was made by immersing a coil of resistance wire enclosed in a glass tube into a Dewar flask two-thirds filled with water. The top of the Dewar flask was closed by means of a large rubber stopper, containing four holes, sealed to the flask with sealing wax. Two of the holes in the stopper served to hold the heating coil, the third was for the delivery tube, and the last for a siphon tube used to supply water to the generator on long runs. Regulating the power supplied to the heating coil served to regulate the flow of steam. The steam could not be metered readily and all that was known was that it was flowing at such a rate that a 3 to 10 fold excess would pass over the sample as evidenced by the collection of condensate in a calibration run.

The Muffle Furnace

The roasting of ore for the filtration and uranium recovery studies was conducted in a muffle furnace in stainless steel trays. The temperature was measured by means of a chromel-alumel thermocouple but it varied considerably from point to point ($\pm 20^\circ\text{C}$) even in an empty furnace. The air was regulated by a valve in the high pressure line. The volume of air was regulated to approximately a three-fold excess of air over the amount calculated to convert the sulfur in the ore to SO_2 .

The Filtration Apparatus

The ore slurries were filtered through a perforated stainless steel cylinder, covered with Vinyon 114, and rubber stoppered at both ends. A glass tube passing through both stoppers enclosed the shaft from an electric stirrer. Through the upper stopper a tube leading from just above the lower stopper carried the filtrate to a calibrated container inside an evacuated bell jar held at 27 in. of mercury vacuum. The beaker containing the slurry was water jacketed and held between 89°C and 91°C . The time for a standard volume of filtrate to be collected was measured with a stop watch. Duplicate runs checked within $\pm 5\%$.

Experimental

Preliminary experiments on the removal of sulfur from pitchblende ores were conducted in glass U tubes. The weighed sample was placed on the bottom of the U, and air was forced through the sample which was heated over an Argand burner. The acid exit gases were caught in an excess of standard sodium hydroxide solution. The excess caustic was titrated with standard hydrochloric acid and the amount of sulfur removed calculated from these figures. This method showed that over 60% of the sulfur could be removed.

Further experiments were conducted in the tube furnace described above. With this apparatus we were able to obtain fairly accurate data on sulfur removal in relation to time and temperature of roast, bed depth, and air flow. With the addition of the electrically heated steam generator and wrapping the exposed portions of the quartz tube with a steam coil to avoid condensation we were able to collect some data on the removal of sulfur by steam.

The data obtained in these experiments may be found in Table I. These data show that increasing the temperature of the air roast increases the sulfur burnout. The length of roast has a much smaller effect on the sulfur removal than does the temperature. A roast in steam does not differ appreciably from a roast in air in sulfur removal (Graphs No. 1 and No. 2). However, increasing the air flow and spreading the ore into a thinner bed both lead to increased sulfur removal (Graph No. 3). On a plant scale a stirred bed would be recommended.

Filtration and uranium recovery studies were conducted on larger samples roasted in trays in the muffle furnace described above. The temperature and air flow could not be controlled as closely throughout the whole bed as in the small samples run in the tube furnace. This was especially evident in high sulfide ores where non-uniform color and caking were found after roasting.

The roasted ore obtained in this way was digested hot in 45% nitric acid then adjusted to a definite slurry density, slurry volume, and excess acid concentration. The slurry obtained was filtered on the small laboratory filter leaf.

The filter cake obtained in the filtration study was exhaustively washed with water and then divided into two or more portions. One portion was given a carbonate leach by stirring at 450 g/l of wet solids, in a solution containing 120 g/l Na_2CO_3 and 90 g/l NaHCO_3 , for 1 hour at 80° C. The other portions were treated at 450 g/l of wet solids with various strengths of acid and other reagents for various lengths of time at or near the boiling points. After filtration the cakes obtained were again exhaustively washed with water and then the insoluble uranium remaining in these cakes determined by the standard control method.

The data obtained from these experiments can be found in Table II. A study of these data show that after roasting and after a carbonate leach of the filter cake, the insoluble uranium left in the washed cake is much too high. Some acid leaches will reduce the insoluble uranium to less than half the amount left in by a carbonate leach. However, the roasted ores hold more uranium in an insoluble form than unroasted ores in all cases. The amount of insoluble uranium held in the roasted ores is a function of the temperature as can be seen in Graph No. 4.

The data on filtration rates and acid consumption are not conclusive. Increasing the temperature of air roasts shows a trend toward substantial increases in filtration rates for most ores. Increasing the temperature of the steam roasts shows a trend toward decreasing filtration rates in most cases. See Graph No. 5. The acid consumption of roasted ores is so variable that no conclusions can be drawn.

Table I

Sulfur Removal Roasts

Ore Lot No.	% S in Ore	% S Removed	Roast Time in Hours	Roast Temp. °C	Roast Gas	Gas Rate cc/min	Remarks
A-195	5.09	45.3	1	600	Air	50	Normal Spread
A-195	5.09	44.2	1	600	Steam >	50	Normal Spread
A-195	5.09	46.0	6½	600	Air	50	Normal Spread
A-195	5.09	62.5	¼	700	Air	50	Normal Spread
A-195	5.09	63.5	½	700	Air	50	Normal Spread
A-195	5.09	67.0	1½	700	Air	50	Normal Spread
A-195	5.09	68.0	1½	700	Air	50	Normal Spread
A-195	5.09	68.3	1½	700	Steam >	50	Normal Spread
A-195	5.09	49.8	1½	700	Nitrogen	50	Normal Spread
A-195	5.09	73.7	3	700	Air	50	Normal Spread
A-195	5.09	68.8	6	700	Air	50	Normal Spread
A-195	5.09	71.1	6	700	Air	50	Normal Spread
A-195	5.09	69.2	6	700	Air	50	Normal Spread
A-195	5.09	77.0	1	800	Air	50	Normal Spread
A-195	5.09	79.0	2	800	Air	50	Normal Spread
A-195	5.09	92.0	6	800	Air	50	Normal Spread
A-204	1.23	93.5	1½	700	Air	50	Normal Spread
A-197	1.38	100.5	1½	700	Air	50	Normal Spread
A-198	4.03	70.0	1½	700	Air	50	Normal Spread
A-205	8.30	71.1	1½	700	Air	50	Normal Spread
A-208	10.04	71.2	1½	700	Air	50	Normal Spread
A-227	6.57	72.9	1½	700	Air	50	Normal Spread, Coarse Grind
A-227	6.57	68.0	1½	700	Air	50	Normal Spread
A-227	6.57	68.3	1½	700	Steam >	50	Normal Spread
A-228	8.87	66.1	1½	700	Air	50	Normal Spread
A-228	8.87	67.9	1½	700	Steam >	50	Normal Spread
A-227	6.57	51.8	1½	600	Air	50	Normal Spread
A-227	6.57	54.5	1½	600	Steam >	50	Normal Spread
A-227	6.57	44.2	1½	500	Steam >	50	Normal Spread
A-227	6.57	30.5	1½	400	Steam >	50	Normal Spread
A-227	6.57	87.9	1½	700	Air	75	Spread Thin (App. 1 5 N)
A-228	8.87	79.9	1½	700	Air	75	Spread Thin
A-227	6.57	76.2	1½	700	Air	50	Spread Thin
A-227	6.57	93.3	1	700	Air	500	Spread Thin
A-227	6.57	95.6	2	700	Air	500	Spread Thin
A-227	6.57	66.8	1	600	Air	500	Spread Thin
A-227	6.57	57.7	1	500	Air	500	Spread Thin

Table II

Filtration & Recovery Studies

Ore Lot No.	Temp. °C	Roast Time hr.	Atmos-phere	Acid Con- sumption HNO ₃ /Ore	Fil- tration Rate gal/hr/ ft ²	CO ₂ Method Time hr	% U in dry Residue	Digest Cake Treatment Treatment as Indicated		
								Treatment	Time hr	% U in dry Residue
A-195				0.85	16	1	0.04*	6N H ₂ SO ₄	5	0.02
A-195								6N H ₂ SO ₄ + KClO ₃	5	0.05
A-195	600	3	Air			1	0.17			
A-195	600	3	Steam	0.79	8	1	0.07			
A-195 (X-fine)	700	3	Air	0.84	16	5	0.19	6N H ₂ SO ₄ + KClO ₃	11	0.17
A-195 (X-fine)	700	3	Steam	0.85	1.8	1	0.09			
A-195	700	3	Air	0.89	33.5					
A-195	700	6	Air			1	0.51	6N H ₂ SO ₄ + 1N H ₃ PO ₄	6	0.15
A-195	700	6	Air					6N H ₂ SO ₄ + HF	6	0.07
A-195	800	1/2	Air			1	0.21			
A-198	600	3	Air	0.73	13	1	0.20	8N HCl + HF	6	0.04
A-198	700	1	Air	0.62	15	1	0.45	Conc. H ₂ SO ₄	3	0.11
A-198	700	3	Air	0.69	18.5	1	0.46	12N H ₂ SO ₄	3	0.18
A-198	700	3	Air					2N H ₂ SO ₄ + MnO ₂	4	0.21
A-198	700	6	Air	0.64	25	1	0.38	8N HCl	4	0.20
A-198	800	1/2	Air			1	0.42			
A-198	800	3	Air	0.50	110	1	1.10	12N H ₂ SO ₄	3	0.45
A-198	800	3	Air					Conc. H ₂ SO ₄	3	0.45
A-198				0.56	10					
A-227	600	3	Air	0.53	2.3	1	0.36			
A-227	600	3	Steam	0.83	12.6	1	0.09			
A-227	700	3	Air	0.45	23.	1	1.34	8N HCl + KClO ₃	6	0.27
A-227	700	3	Steam	0.81	7.0	1	0.11	6N H ₂ SO ₄	6	0.08
A-227	800	3	Air	0.42	9.7	1	3.70			
							7.20	CO ₂ + oxid. agent	5	3.68
A-227	800	3	Steam	0.78	2.5	1	0.16	6N H ₂ SO ₄	6	0.10
A-228	600	3	Steam	0.78	1.7	1	0.05			

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Table II(Cont'd)

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Filtration & Recovery Studies

Ore Lot No.	Temp. °C	Roast Time hr.	Atmos- phere	Acid Con- sumption HNO ₃ / Ore	Fil- tration Rate gal/hr/ ft ²	Digest Cake Treatment		
						Treatment as Indicated		
						CO ₂ Method Time hr	% U in dry Residue	% U in dry Residue
A-228	700	3	Steam	0.83	2.8	1	0.10	
A-228	700	3	Air	0.53	1.8	1	1.02	
A-228	800	3	Steam	0.80	3.1	1	0.16	
A-228				0.96				
A-218						1	0.03*	
A-218	700	3	Air			1	0.20	
A-232						1	0.03*	
A-232	700	3	Air			1	0.33	

*These are typical of residues from pitchblende

GRAPH No. 1

SULFUR REMOVAL vs ROAST

Ore Lot A-195

O = Air Roast

Δ = Steam Roast

□ = Nitrogen Roast

GRAPH No. 2

Sulfur Removed vs Sulfur Present in Ore

Roasted $1\frac{1}{2}$ hr. @ 700°C.

- Roasted in Air
▽ " " Steam
□ " " Nitrogen

GRAPH No. 3

EFFECT OF AIR FLOW & BED THICKNESS

Residue

GRAPH No. 5

FILTRATION RATE vs ROAST TEMP

2 hr. Roast except as noted

Filtration Rate gal/hr./sq. ft.