Kinetics of Cobalt and Manganese Precipitation from Acid Mine Drainage Using Ozone

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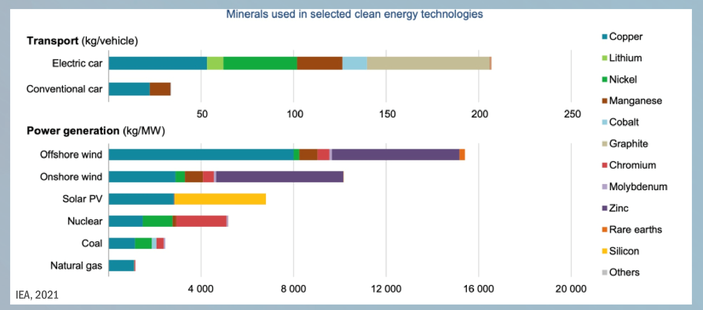
INTRODUCTION

- Cobalt (Co) and Manganese (Mn) are listed as critical elements by the U.S. Department of Interior.
- U.S. is currently 100% and 78% reliance on foreign sources of Mn and Co, respectively.
- Major applications and secondary resources:



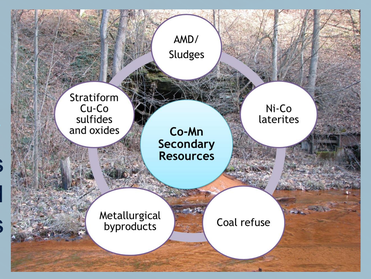
- Acid Mine Drainage (AMD):

$FeS_2 + \frac{7}{2} O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2\,H^+$

$Fe^{2+} + \frac{1}{4} O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2} H_2O$

$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16H^+$

- AMD in the Appalachian region has been found to contain elevated contents of critical elements such as REEs, Al, Co, and Mn.

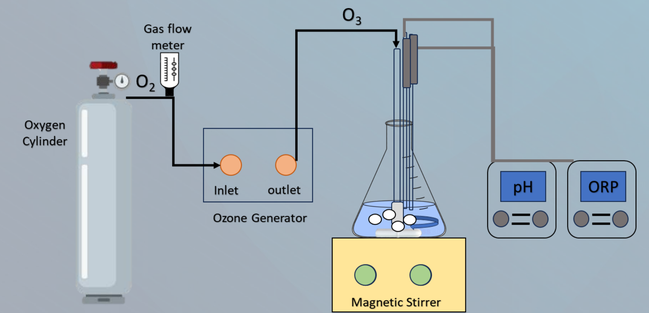


OBJECTIVES

- To investigate the effect of various ligands/oxidants on the precipitation of Co-Mn from AMD, understand the effect of process parameters, Identify the mechanism governing the precipitation of these elements, and determine the kinetics of the process.

MATERIAL & METHODS

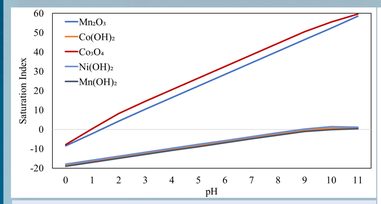
Source	Elemental concentration (ppm)								
	Al	Fe	Mg	Mn	Co	Ni	Cu	Zn	TREE
AMD	45.6	4.7	399.8	41.8	0.9	1.6	0.1	3.1	0.5
Sludge	90550	25725	104621	49096	1325	2371	607	5145	1143



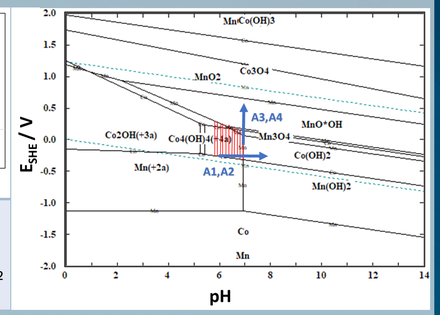
Experimental Setup

SOLUTION CHEMISTRY

Saturation indexes of Co and Mn



Pourbaix diagrams of Co-Mn

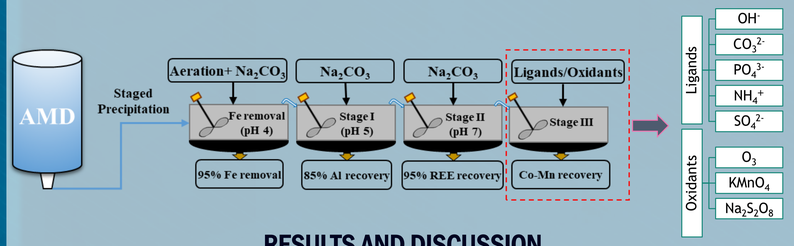


A1: $Mn^{2+} + 2OH^- = Mn(OH)_2$

A2: $Co^{2+} + 2OH^- = Co(OH)_2$

A3: $Mn^{2+} + 1/2O_2 + 3/2H_2O = MnOOH + 2H^+ + 1/2O_2$

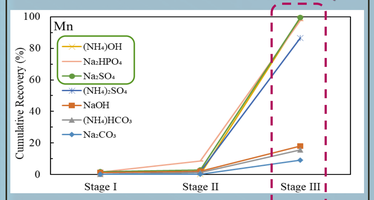
A4: $Co^{2+} + 1/2O_2 + 3/2H_2O = CoOOH + 2H^+ + 1/2O_2$



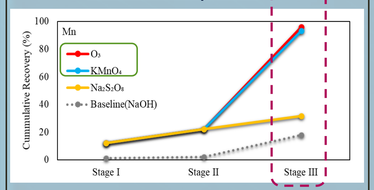
RESULTS AND DISCUSSION

Precipitation

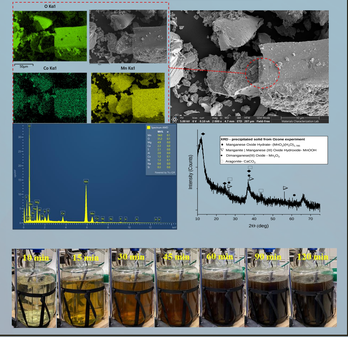
Ligand Precipitation



Oxidative Precipitation

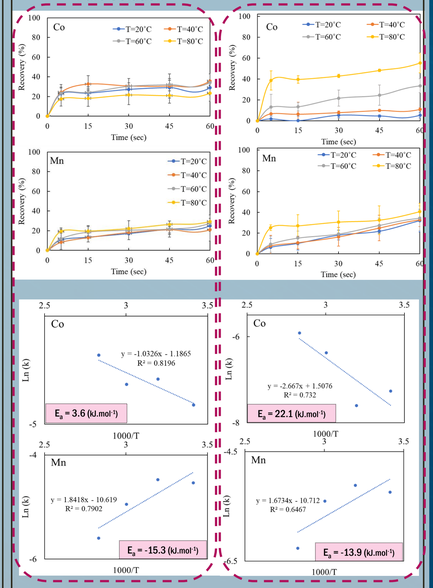


Sample Characterization

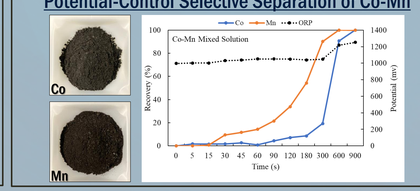


Kinetic Study

Effect of Temperature on Oxidative Precipitation



Potential-Control Selective Separation of Co-Mn



PARAMETRIC STUDY

Co

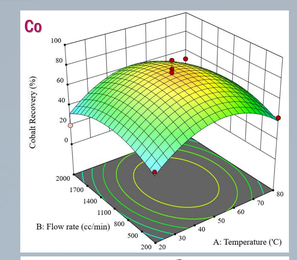
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4303.47	4	1075.87	9.11	0.0013	significant
A-Temp.	86.00	1	86.00	0.7285	0.4101	
B-Flow rate	0.5101	1	0.5101	0.0043	0.9487	
A^2	3027.98	1	3027.98	25.65	0.0003	
B^2	984.15	1	984.15	8.34	0.0136	
Residual	1416.72	12	118.06			
Lack of Fit	1094.95	8	136.87	1.70	0.3190	not significant
Pure Error	321.77	4	80.44			
Cor Total	5720.19	16				

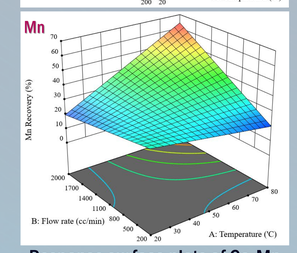
Mn Optimum Conditions:
flow rate = 700 (cc/min); Temperature = 80 ºC

Mn

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1887.33	5	377.47	4.37	0.0196	significant
A-Temp.	501.81	1	501.81	5.80	0.0347	
B-Flow rate	16.16	1	16.16	0.1869	0.6739	
C-Stirring rate	56.13	1	56.13	0.6491	0.4375	
AB	798.63	1	798.63	9.24	0.0113	
BC	514.61	1	514.61	5.95	0.0328	
Residual	951.13	11	86.47			
Lack of Fit	550.62	7	78.66	0.7856	0.6348	not significant
Pure Error	400.51	4	100.13			
Cor Total	2838.47	16				

Co Optimum Conditions:
flow rate = 1100 (cc/min); Temperature = 50 ºC





Response surface plots of Co-Mn Oxidative Precipitation

CONCLUSIONS

- Among various ligands and oxidants, ozone resulted in the highest recovery/grade for Mn (98%/82.9%) and Co (99%/1.4%).
- In the proposed staged precipitation process, more than 95% of Co-Mn, 95% of REE, and 85% of Al were recovered.
- Temperature and flow rate were the significant parameters in recovery of Co, while flow rate and its interactive effect with temperature, and with stirring rate emerged as the significant parameters in recovery of Mn.
- The activation energy values suggest that the oxidative precipitation of Co and Mn is most likely a diffusion-controlled process.

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