A New Technology for **Acid Mine Drainage Treatment**

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NORAM Engineering and Constructors Ltd.

NORAM Engineering & Constructors Ltd.

- Specializes in the development and commercialization of chemical processes.
- Developed the worlds leading technology for the manufacture of Nitrobenzene with 6 world scale plants built and operating.
- Recent development projects include:
  - Waste-water treatment process for removing mercury and other heavy metals from groundwater.
  - Stabilisation product to stabilise leachable mercury contaminated soils.
  - Efficient compact hydrogen reformer for use in fuel cells.
- Privately owned BC company established in 1988. with approx. 80 employees.
- 40% ownership in BC Research.

Pros and Cons of pH modification using lime

PROS

- Tried and tested
- Effective
- Unaffected by seasonal temperatures.
- Relatively simple operation procedures.
- Can accommodate change in water quality and quantity.

CONS

- High pH is needed to remove metals such as manganese may cause remobilization of other metal hydroxides (e.g. aluminum)
- Large amounts of lime are used. Manufacture of lime causes co2 emissions. (greenhouse gases).
- Large volumes of sludge are generated, which are expensive to handle and difficult to dispose of.
- Sludges generally have no commercial value and are commonly stored on site in storage ponds.
- Environmental liability still remains with stored sludge.

Active treatment technologies for AMD

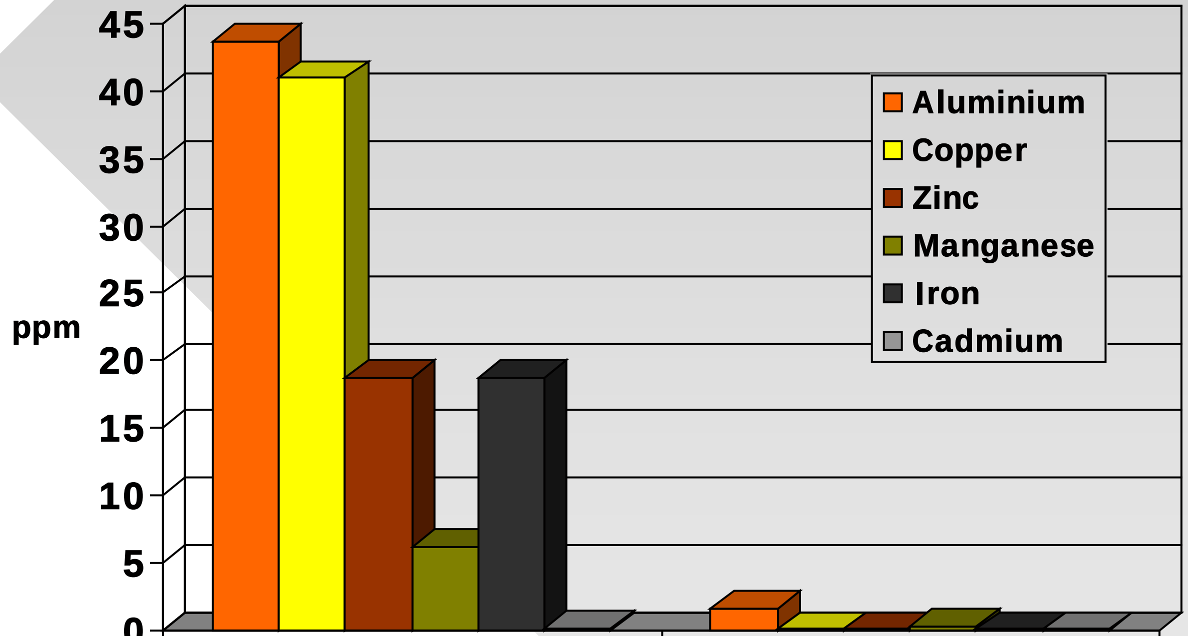
- pH modification.
- Ion Exchange.
- Biology-based technology.
- Other adsorption technologies.
- Electrochemical technology.
- Physical process technology.

Lignor™ - AMD Process

- Development based on a Noram technology using humic and fulvic acids for the recovery of mercury from the groundwater at a large remediation project in Squamish BC.
- The Lignor™ Process simulates the chelating properties of humic and fulvic acids using lignin derivatives.
- Lignin derivatives/ lime/caustic soda/air oxidation. Plus optional ferric addition for further metal removal.
- Produces less sludge volume which is easily dewatered.
- Cost of reagents are reduced.

Metal Removal Trial Results
(no ferric addition)

- **Effluent quality of lignor™-AMD process are excellent.**

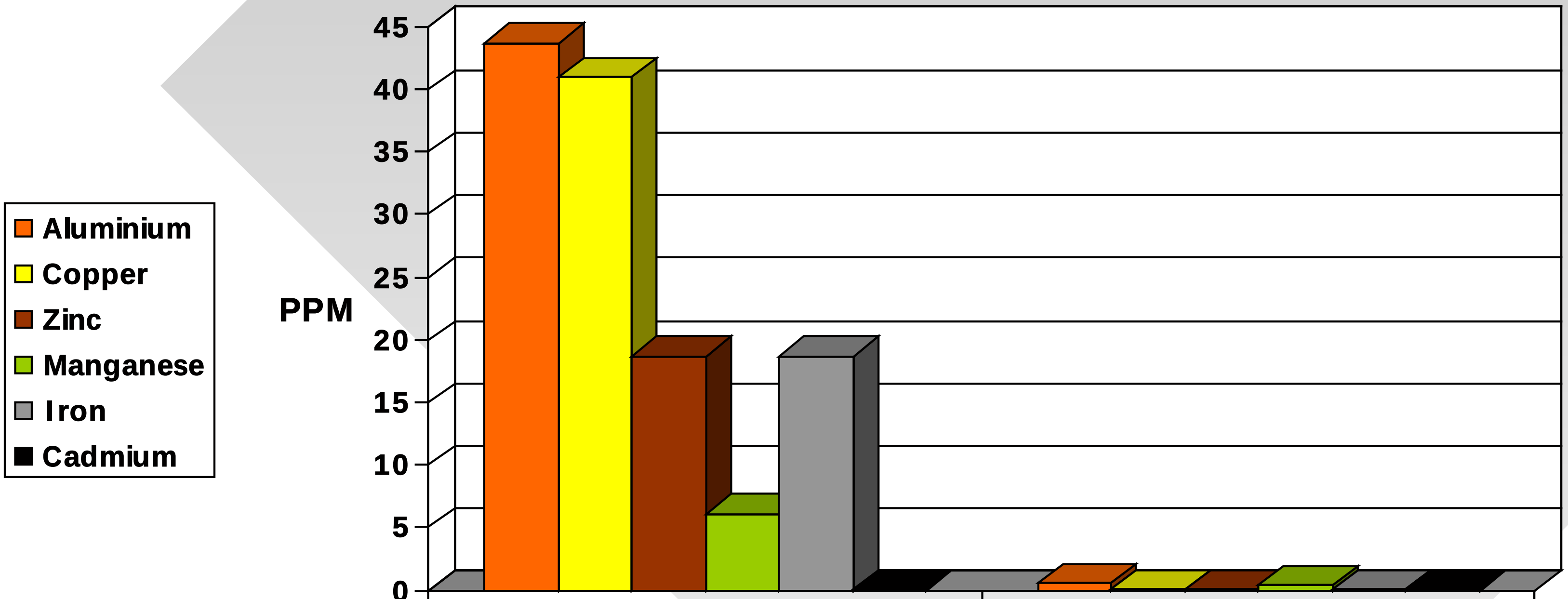


	Lignor run #7 before	Lignor run #7 after
Aluminium	43.7	1.59
Copper	41	0.04
Zinc	18.7	0.02
Manganese	6.125	0.257
Iron	18.7	0.02
Cadmium	0.098	0.003

Metal Removal Trial Results

(Ferric addition)

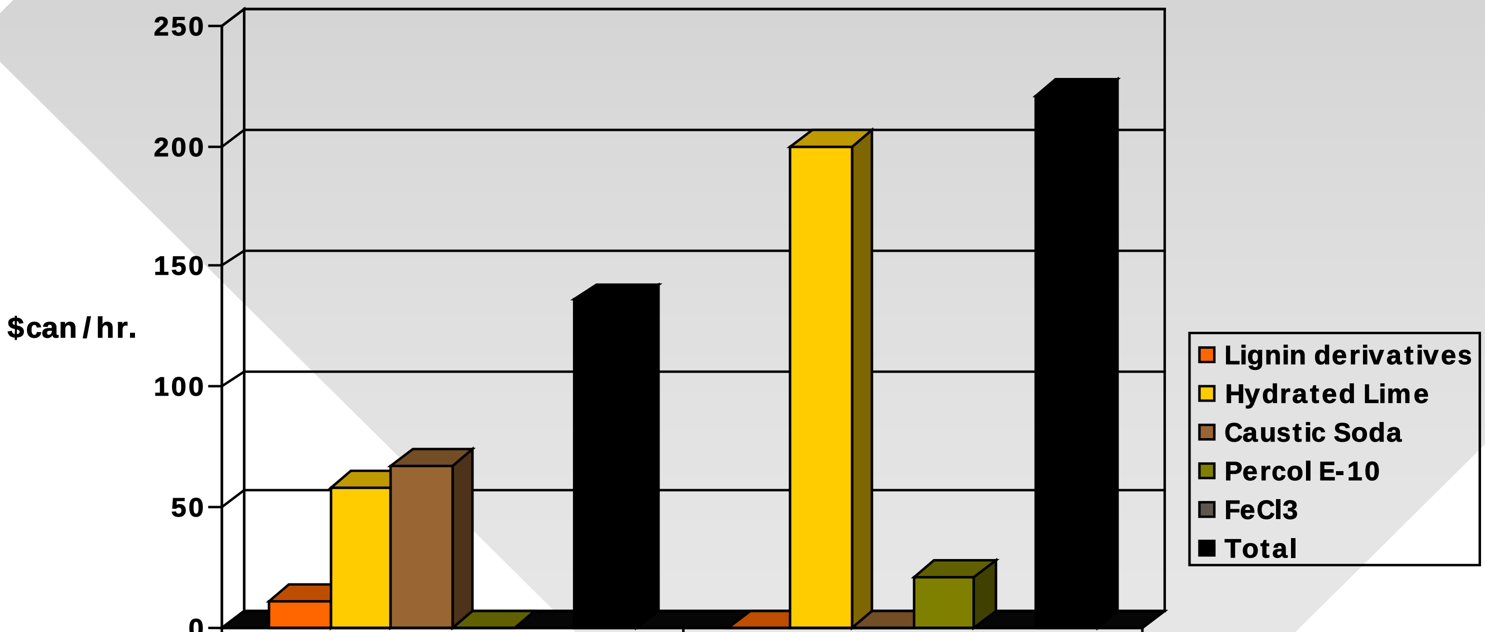
• **Addition of Ferric reduces aluminum, improving effluent quality**



	Lignor run #13 before	Lignor run #13 after
Aluminium	43.7	0.58
Copper	41	0.03
Zinc	18.7	0.032
Manganese	6.125	0.338
Iron	18.7	0.02
Cadmium	0.098	0.005

Reagent costs

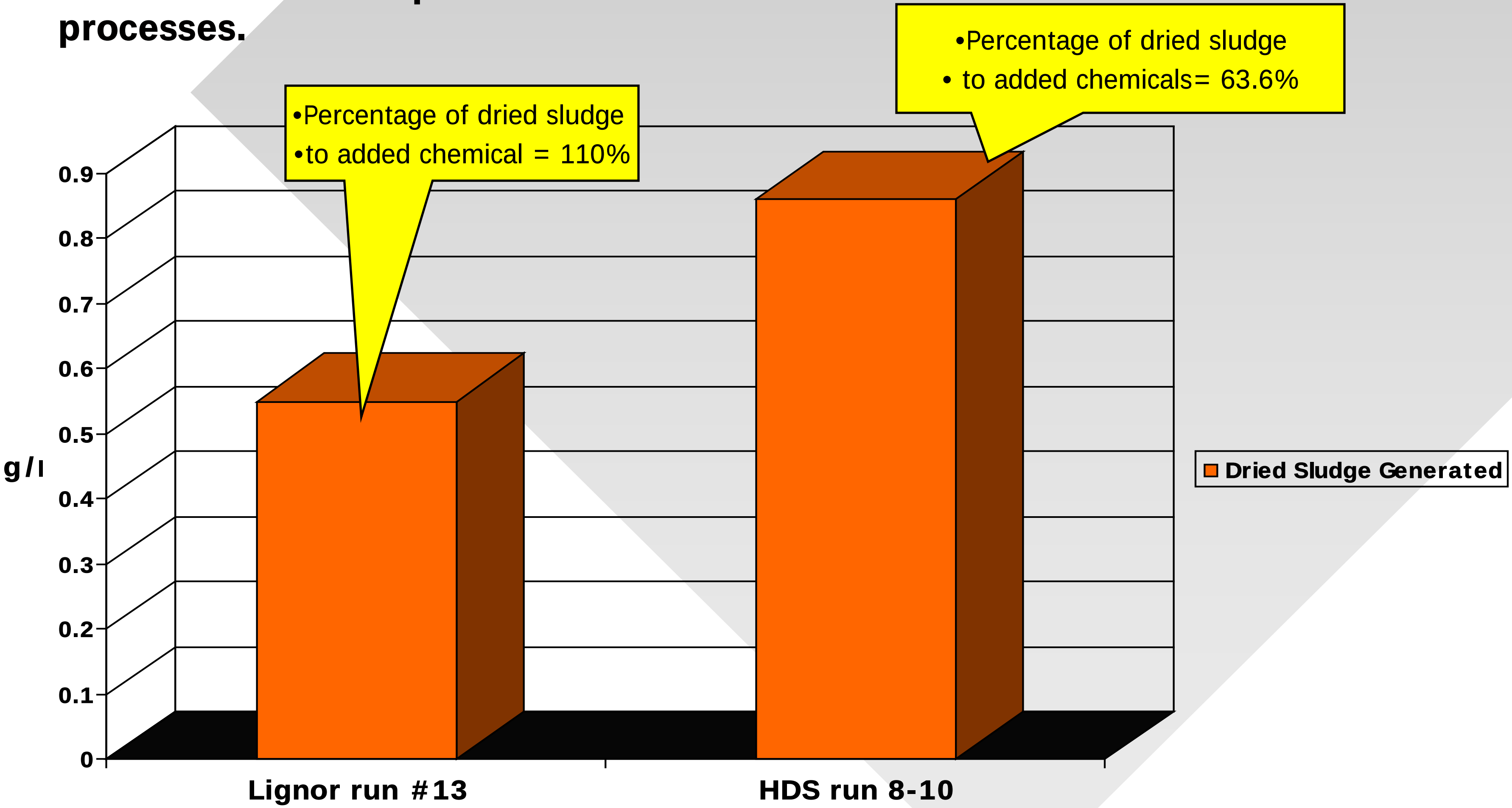
- Lignor™ process has the potential to save 36% costs of reagents, over other ph modification processes.



	Lignor run #13	HDL run 8-10
Lignin derivatives	11	0
Hydrated Lime	58	200
Caustic Soda	67	0
Percol E-10	0	21
FeCl3	not included	not included
Total	136	221

Sludge Generation

•Lignor™ generates >36% less sludge, than other conventional ph modification processes.



Main Point Summary

- Lab scale research and development has successfully proven the concept of the technology, and the benefits over other available technologies.
- A patent application for the Lignor™-amd process as been filed.
- Lignor™-amd process uses reagents at considerable less cost than other pH modification processes.
- Lignor™-amd process generates sludge that is stable and considerable less voluminous than other ph modification processes.
- Lignor™- amd process produces an acceptable quality effluent.

Next Steps

- Move the status of the Lignor™-AMD Process from an "Emerging Alternative Technology" to an "Available Alternative Technology".
- Develop and engineer a full scale $3m^3$ /hr full scale skid mounted plant.
- Develop and implement an extensive full-scale field testing program.

APPLIED CHEMISTRY
for Lignor^{TM} Process of AMD Treatment

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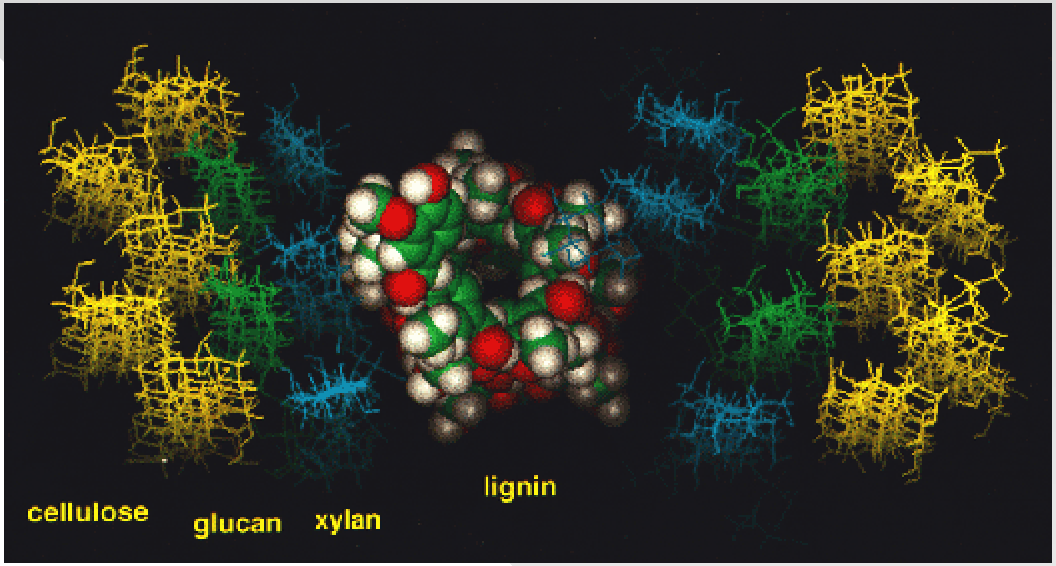
Application of Lignin Derivatives

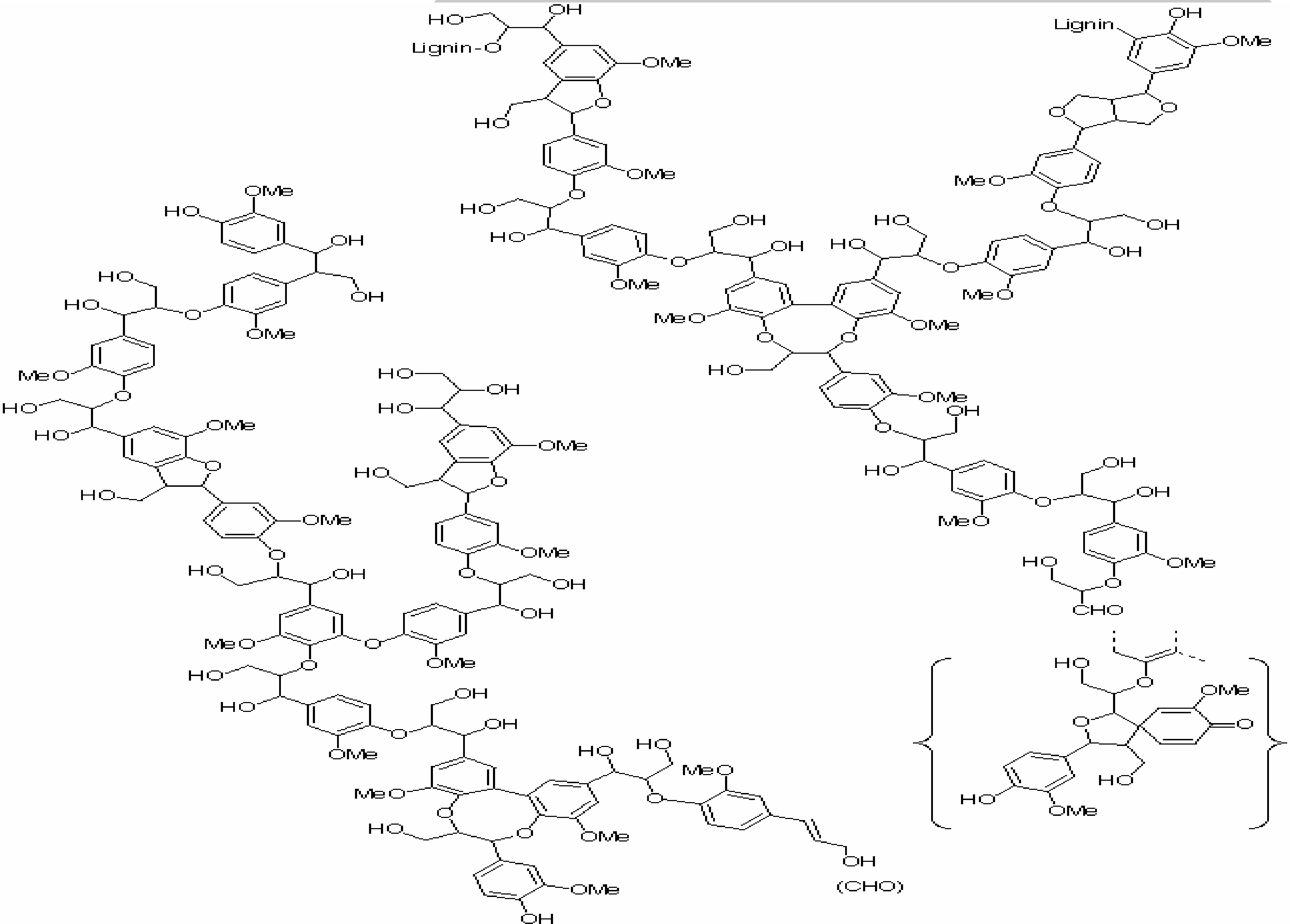
Humic / fulvic acids (HFA) – natural chelating agent.

Lignin - one of the most important precursor of HFA.

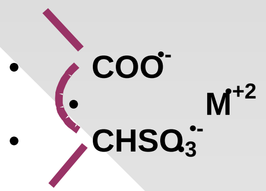
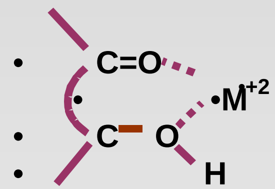
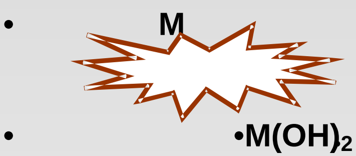


Lignin derivatives – Kraft lignin and lignosulfonates.

The structure of softwood lignin



The Bonding Types between Metal and Lignin Derivatives

•Item	•Chemical Bonded M •Cation •(primary force)		•Physical Adsorbed M •(secondary force)
•Bonding •Type	•Ionic bond	•Coordinate •covalent bond	•Intermolecular force •(Van•der•Waals force)
•Pattern			
•Character	•M Lingnonates	•Metal Complex	•Lignin Derivatives

Benefits of Applying Lignin Derivatives

– Protect lime from developing an external coating on surface, and favor dissociation of hydrated lime.

– Increase particle settling efficiency by: bridging the space between particles through adsorption (Flocculation), promoting consolidation of small particles into larger particles (Coagulation).

– Immobilize metals in sludge.

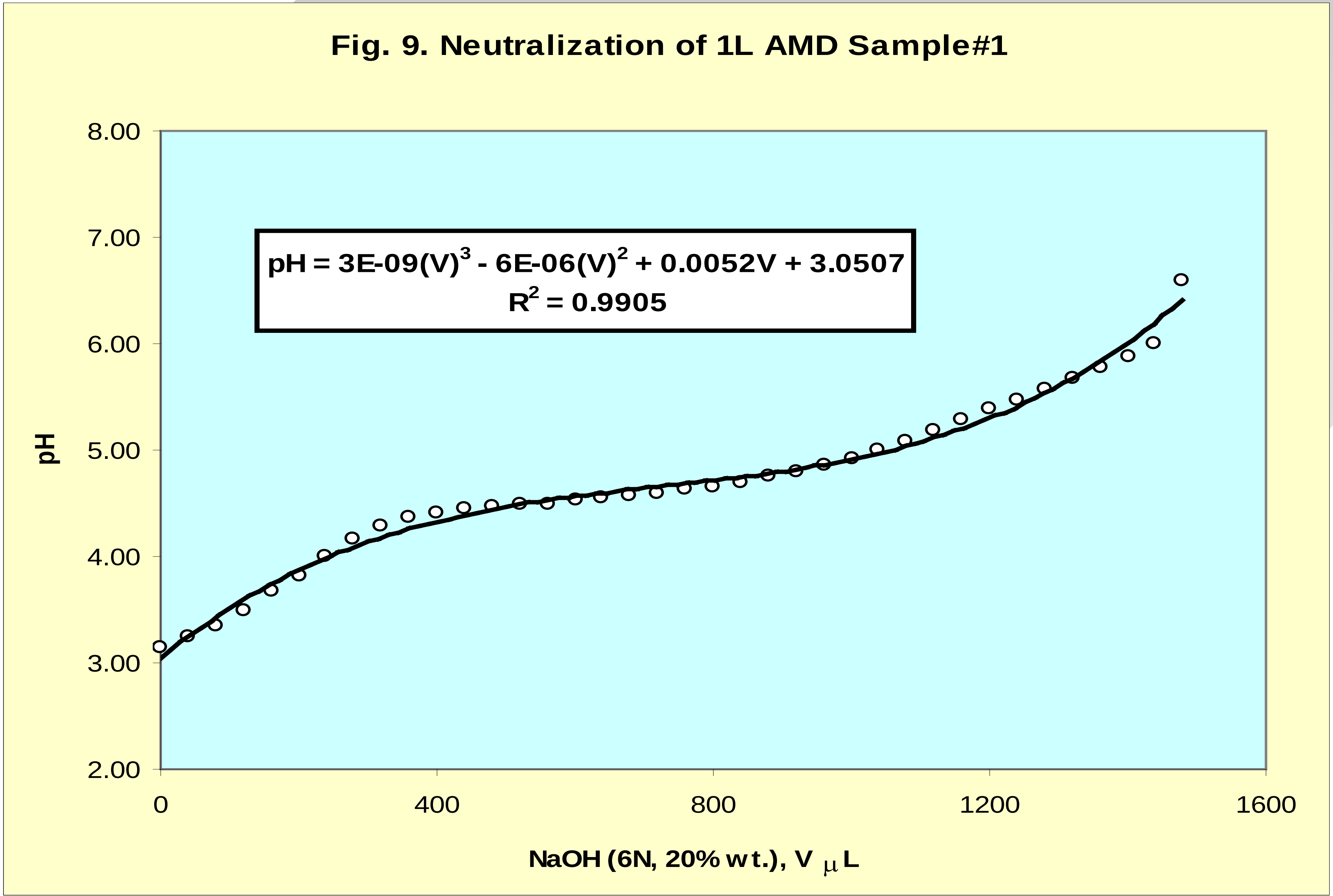
The pH Relation to Metal Hydroxides Precipitation

•pH	•Precipitation of Metal Hydroxides
•5	•$Fe(OH)_3$
•6	•$Al(OH)_3$
•7.5 – 8	•$Cu(OH)_2$
•8.5 - 9	•$Zn(OH)_2$
•9	•$Fe(OH)_2$
•9.5 – 10	•$Cd(OH)_2$
•10 – 11	•$Mn(OH)_2$; •$Mg(OH)_2$
•12	•$Ca(OH)_2$

Alkali Demand of AMD

- Acidity determination by titration with caustic soda.
- Calculation of $CaCO_3$ equivalent for proton acid and mineral acid.

Acidity to pH 8.3 is equivalent to 480mg/L $CaCO_3$, or 355mg/L $Ca(OH)_2$.



Calculation of $CaCO_3$ equivalent for proton acid and mineral acid for AMD at pH 3.2

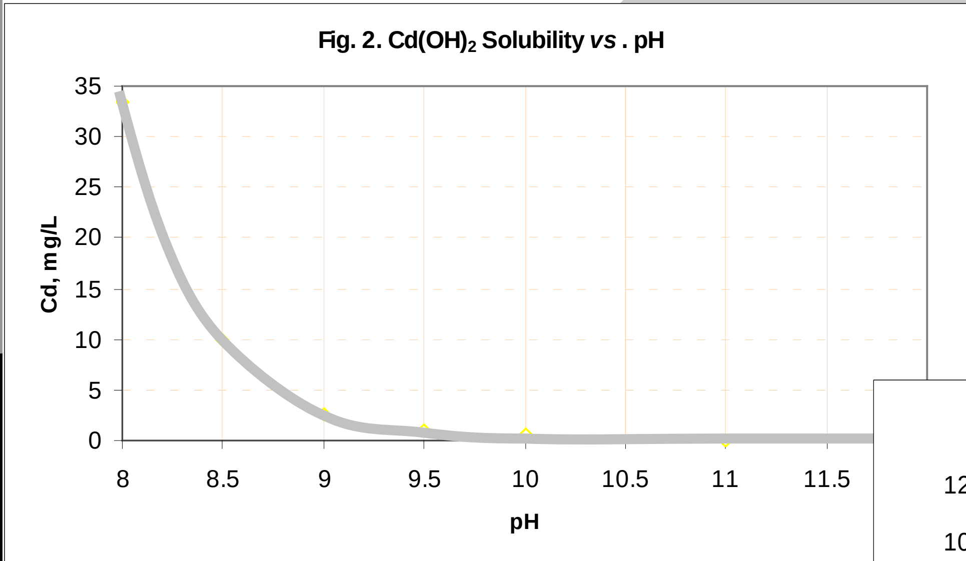
Ions	M.Wt.	Eq.Wt.	Substance to $CaCO_3$ equivalent (multiply by)	AMD			
				Sample #1 (mg/L)	Substance to $CaCO_3$ equivalent	Sample #2 (mg/L)	Substance to $CaCO_3$ equivalent
H	1	1	50.00	0.63	31.5	0.63	31.5
Al	27	9.0	5.56	56.9	316.1	43.7	242.8
Cd	112.4	56.2	0.89	0.100	0.1	0.098	0.1
Co	58.9	29.5	1.70	0.161	0.3	0.137	0.2
Cu	63.4	31.7	1.58	41.0	64.7	28.7	45.3
Fe	55.9	18.6	2.68	17.02	45.7	8.81	23.6
Mn	54.9	27.5	1.35	7.11	13.0	6.12	11.1
Ni	58.7	29.4	1.26	0.1	0.2	0.088	0.1
Pb	207.2	103.6	0.36	0.08	0.0	0.06	0.0
Zn	65.4	32.7	1.13	19.1	29.2	18.7	28.6
				Total $CaCO_3$ eq. = 501mg/L		**Total $CaCO_3$ eq. = 384mg/L**	
$CaCO_3$ equivalent to $Ca(OH)_2$ (multiply by 0.74)							
			Required $Ca(OH)_2$	**371mg/L**		**284mg/L**	

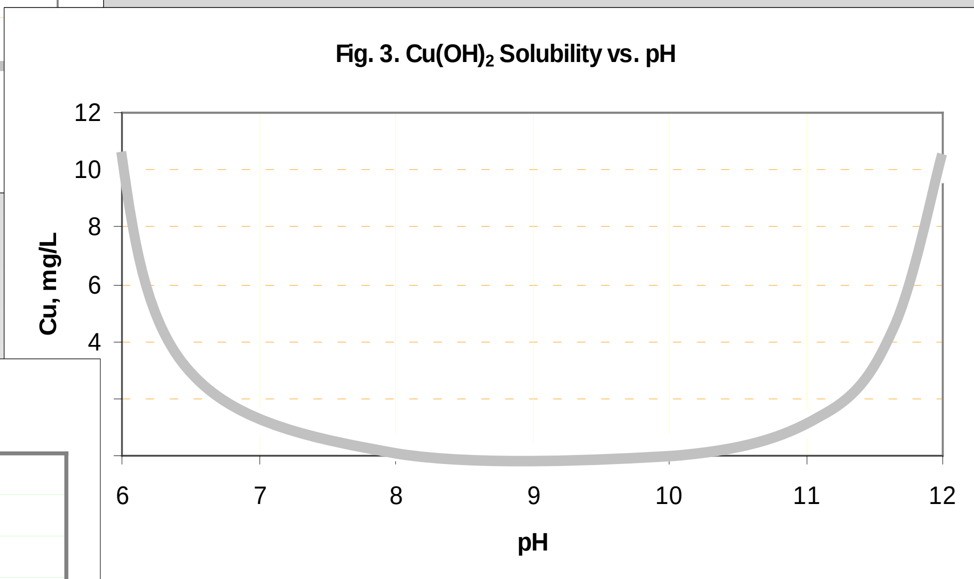
Calculation of Mass Balance for Each Concerned Metal

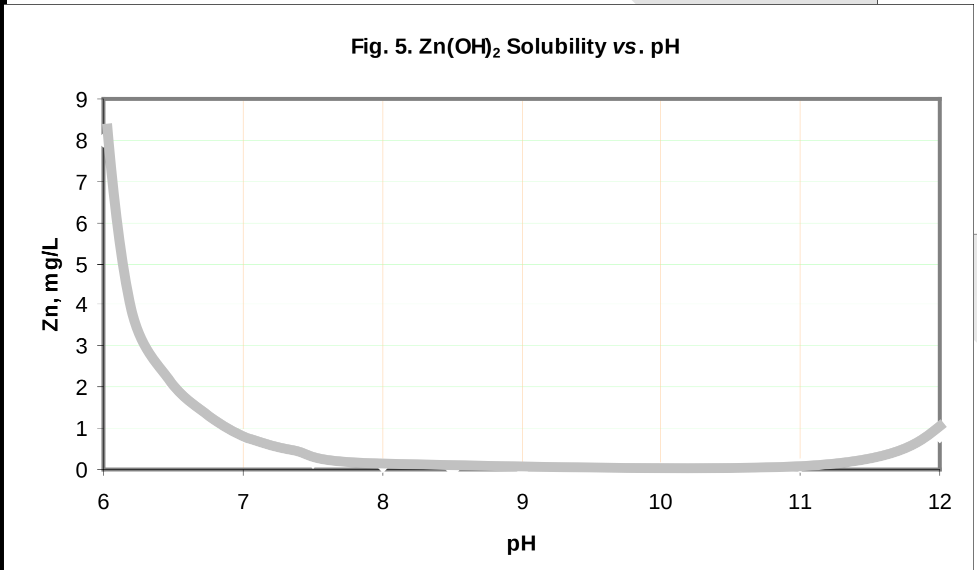
Metals [1]	AMD Sample #2 (mg/L)	Test-13 (mg/L)	Reduction		Test-13-DS[2]		Recovery[4] (%)
			mg/L	%	mg/kg	mg/L[3]	
Al	43.7	0.58	**- 43.1**	**- 98.6**	80900	**44.3**	**102.7**
Ca	335 + 211[5]	422	124[7]	22.7[7]	43700	23.9	19.3
Cd	0.098	0.005	**- 0.093**	**- 94.9**	179	**0.098**	**105.4**
Co	0.137	<0.005[6]	- 0.13	> - 96.4	250	0.137	100 – 104
Cu	28.7	0.03	**- 28.7**	**- 99.9**	49500	**27.1**	**94.5**
Pd	0.06	<0.02[6]	- 0.06	-----	142	0.078	------
Mg	93.1	51.7	- 41.4	- 44.5	70900	38.8	93.7
Mn	6.125	0.338	**- 5.79**	**- 94.5**	10900	**5.96**	**103**
Na	9.94	86	76[7]	[7]	803	0.439	dissolved
Ni	0.088	<0.005[6]	- 0.088	> - 94.3	169	0.092	104 – 111
Zn	18.7	0.032	**- 18.7**	**- 99.8**	32000	**17.5**	**93.7**

Note: (1) Determined by ICP method. (2) Dried Sludge (547mg/L) was collected from Test-13. (3) mg/L = mg/kg * 0.547g/L
(4) Each Metal Recovery (%) = 100*Test-13-DS / (Sample #2 – Test-13). (5) Amount of added agent.
(6) Less than Detector Limit. (7) Increased by added agents.

Metal Precipitation and pH







The Contents of [CO_3^{2-}] Relation to Metal Carbonates Precipitation

[CO_3^{-2}], (mg/L)	Precipitation of Metal Carbonates
0.24	$CdCO_3$
0.40	$ZnCO_3$
0.45	$MnCO_3$
0.60	$FeCO_3$
1.25	$CuCO_3$
6.53	$CaCO_3$
19.8	$MgCO_3$

Metal Precipitation and pH

Fig.1. $Al(OH)_3$ Solubility *vs.* pH

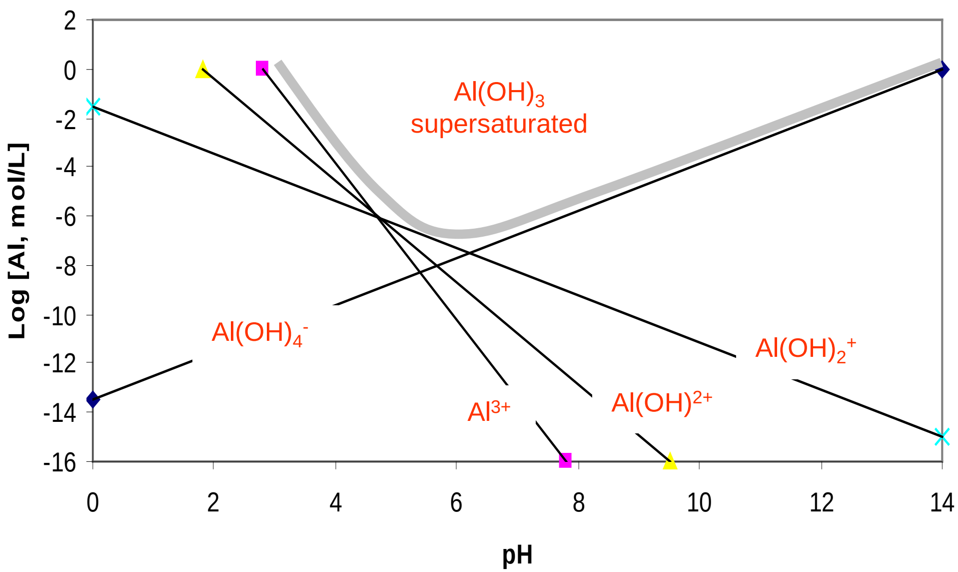
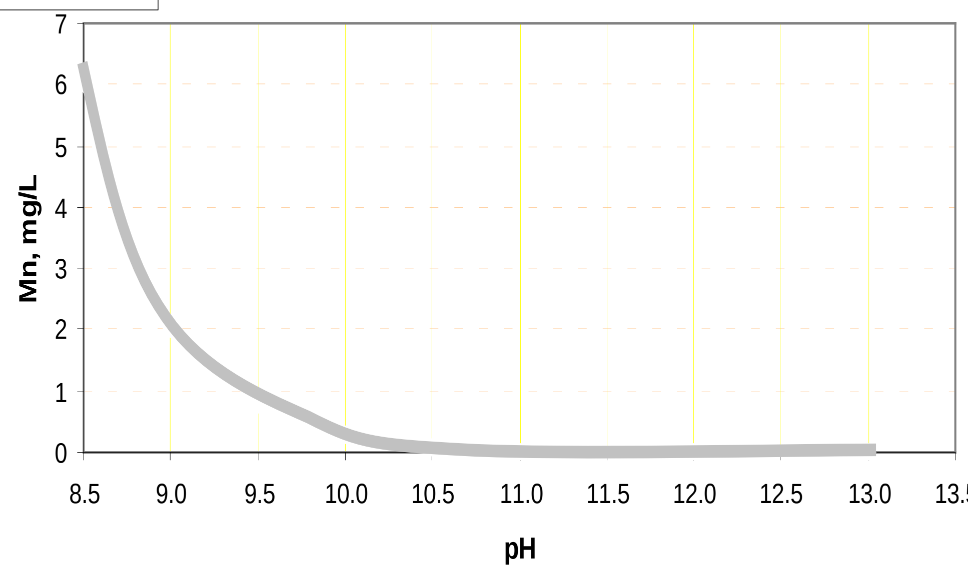
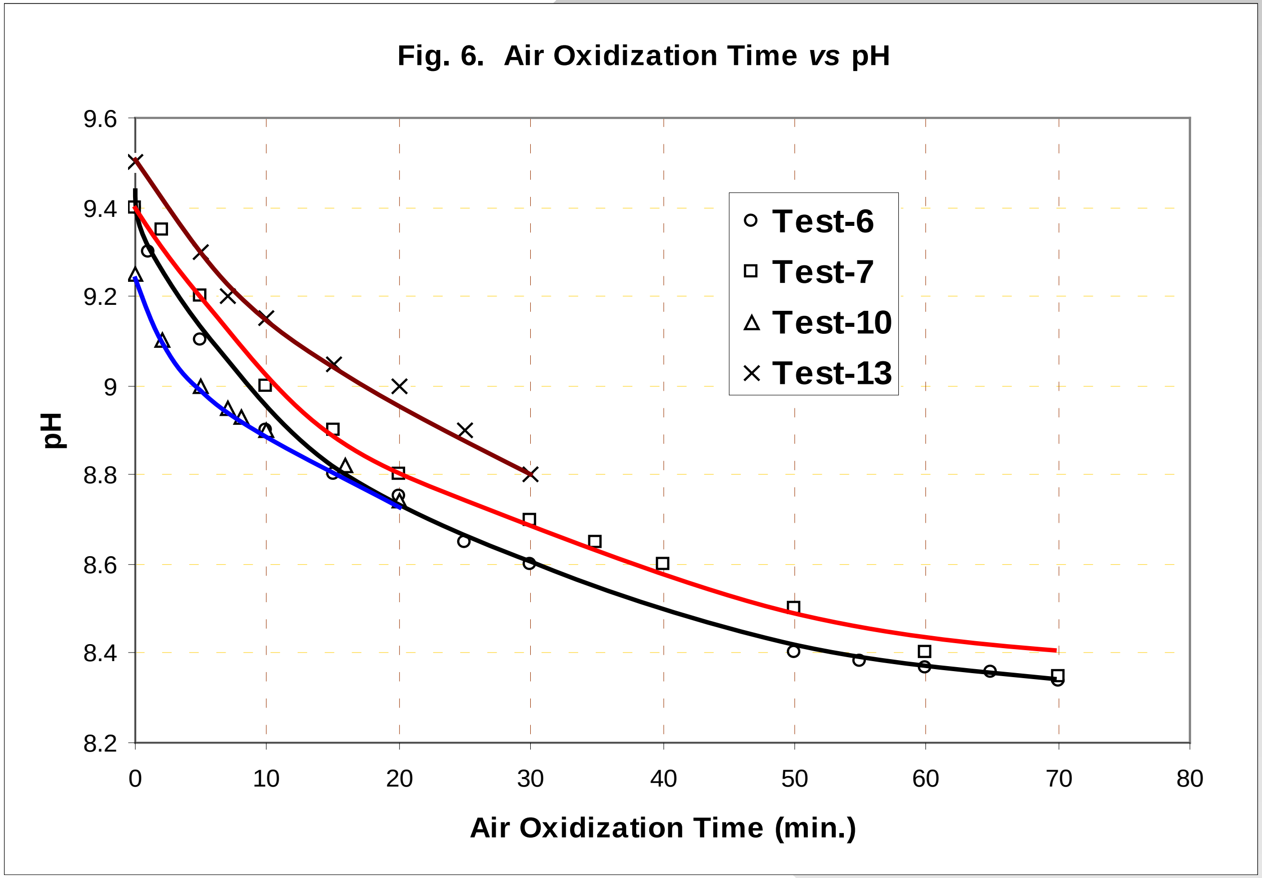


Fig. 4. $Mn(OH)_2$ Solubility vs. pH



Air Oxidation of AMD



$$2\,Mn^{2+} + 2\,H_2O + O_2 \longrightarrow 2\,MnO_2 + 4\,H^+$$

$$4\,Fe^{2+} + O_2 + 4\,H^+ \longrightarrow 4\,Fe^{3+} + 2\,H_2O$$

$$Fe^{3+} + 3\,^-OH \longrightarrow Fe(OH)_3$$

Conclusions

Lignor^{TM} process is composed of:

(1) Application of lignosulfonates,
(2) AMD neutralization by lime to about pH 7,
(3) pH adjustment with caustic soda to 9.4 – 9.6,
(4) air oxidation to drop pH to a desired level, and
(5) small amount of $FeCl_3$ for additional removal of dissolved metals.


QUESTIONS ?
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