Dominant trace metal removal products in a hard rock mine discharge bioreactor

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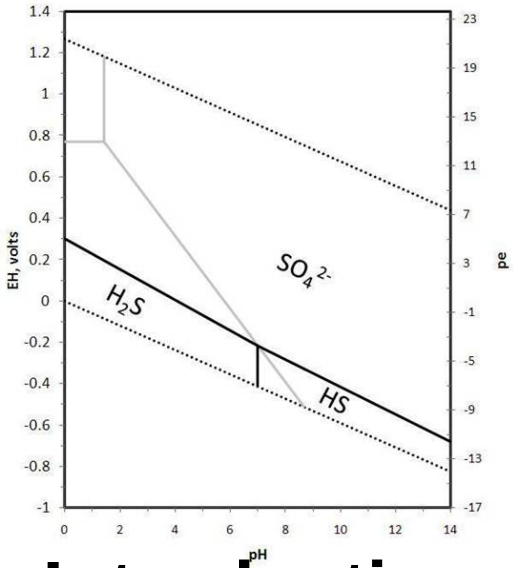
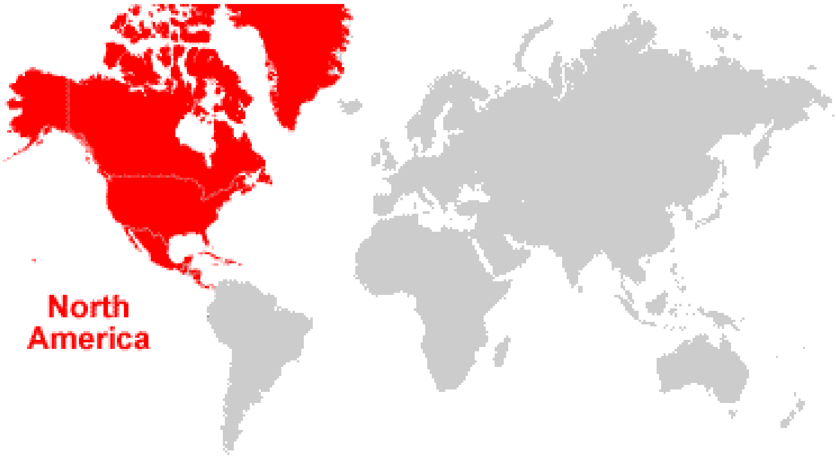
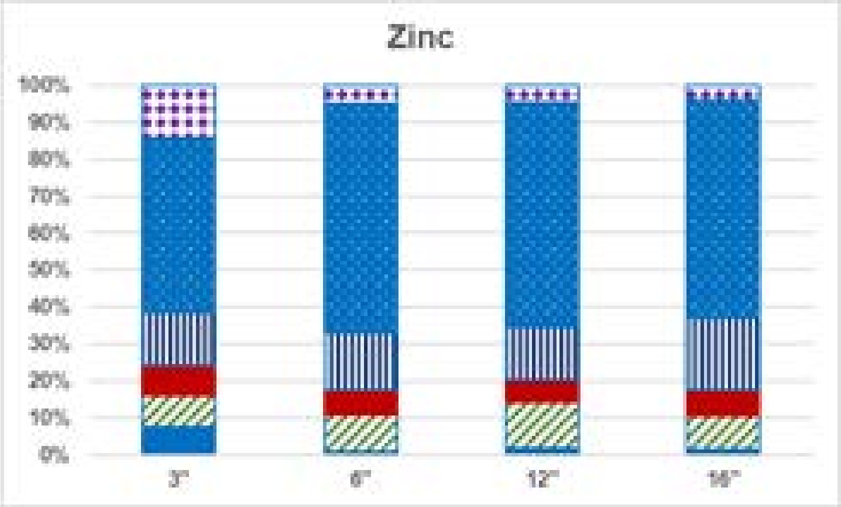


Introduction



Methods



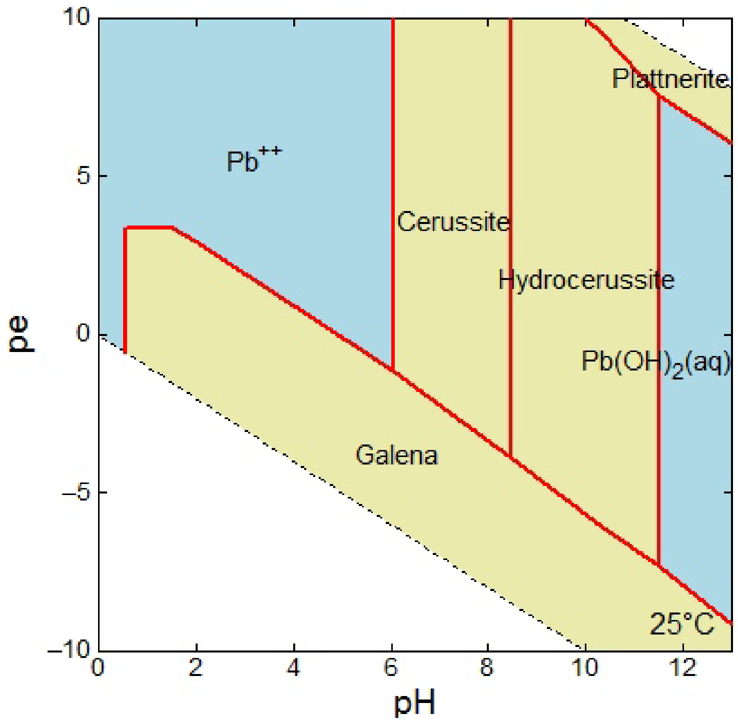
Results and Conclusions

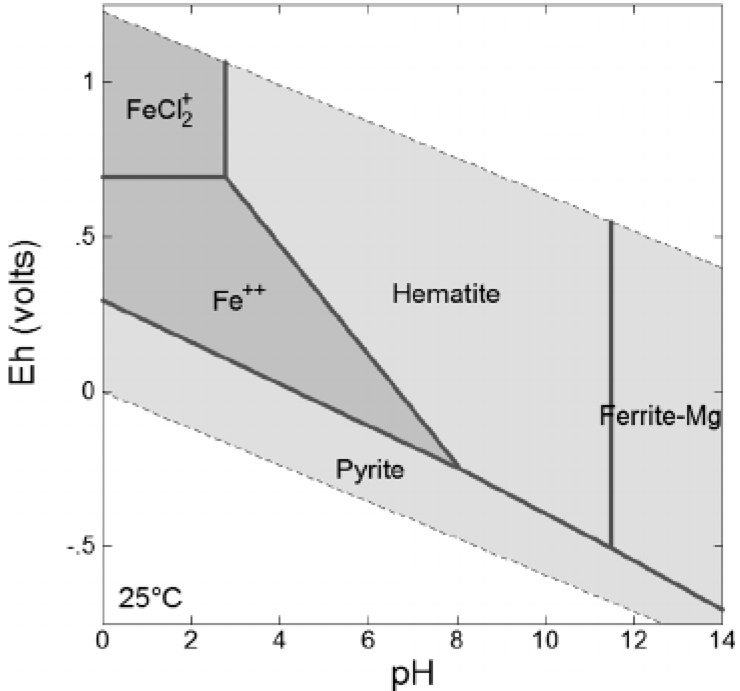
Why bioreactors?

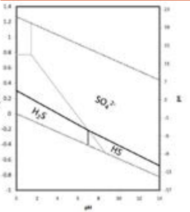
- Produce an anoxic, reducing environment
  - Favorable conditions to reduce abundant sulfate in mine drainage

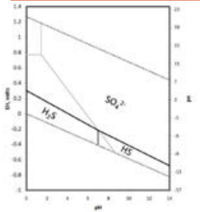
- Sulfate reduction
  - $2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$
  - $H_2S + M^{2+} + HCO_3^- \rightarrow MS\downarrow + 2H_2O + 2CO_2$

- Considered an excellent retention option for Fe, Zn, Pb, Cd, etc.
  - Mn is a notable exception with regard to common mine water constituents



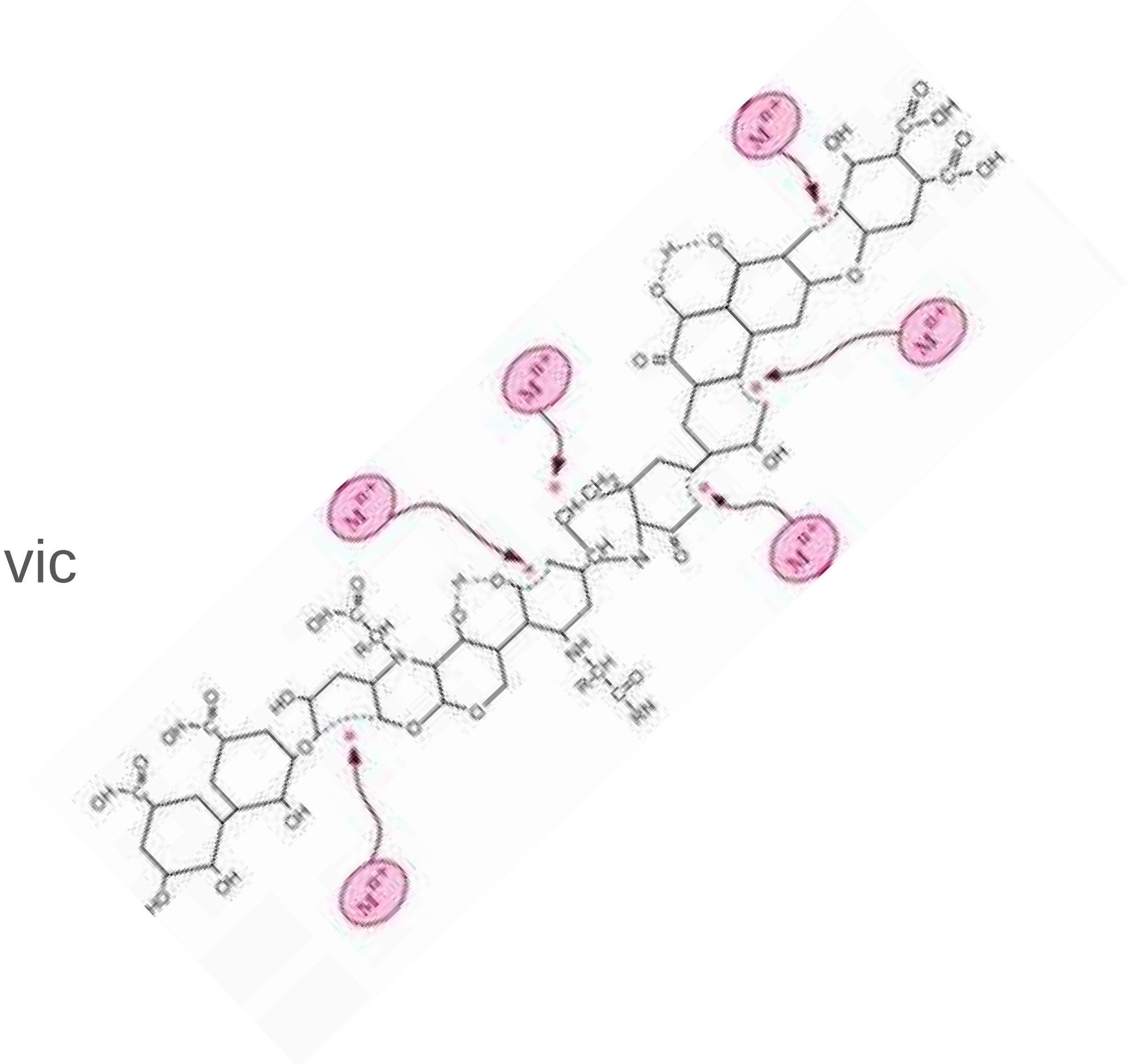




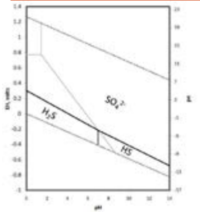


Other removal mechanisms

- Adsorption to organic matter
- Formation of carbonates
  - Or substitution of Ca in calcite
- Complexation with organic matter
  - Highly degradable (humic and fulvic acids)
  - Low TOC:TN
- Association with refractory organic matter
  - Decay resistant
  - Very high TOC:TN

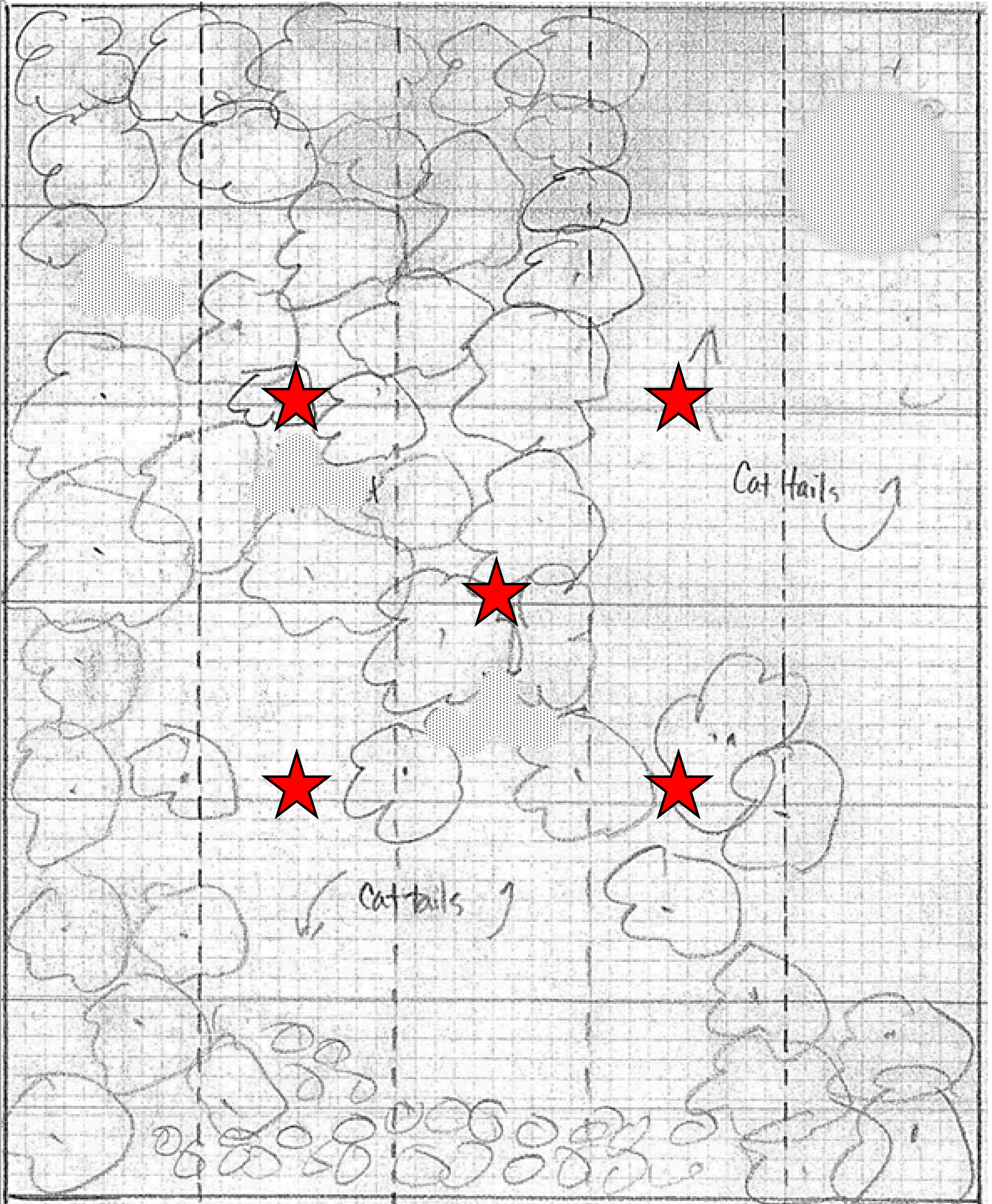


Goals of this project



- Evaluate removal products in a bioreactor that had been in operation for ~10 years
  - In the process of being decommissioned
- Look at removal product as a function of depth in substrate
  - Assumption is that as we move deeper into the substrate, percentage of metals removed as sulfides will increase

Methods



- ~29m x 41 m
- ~1.7 m deep
  - 63% aged chipped wood
  - 3% manure
  - 5% agricultural limestone
  - 29% loose alfalfa hay

- Standing water in most locations

- Vegetation allowed to grow in substrate
  - Dominated by cattails and willows

Sampling

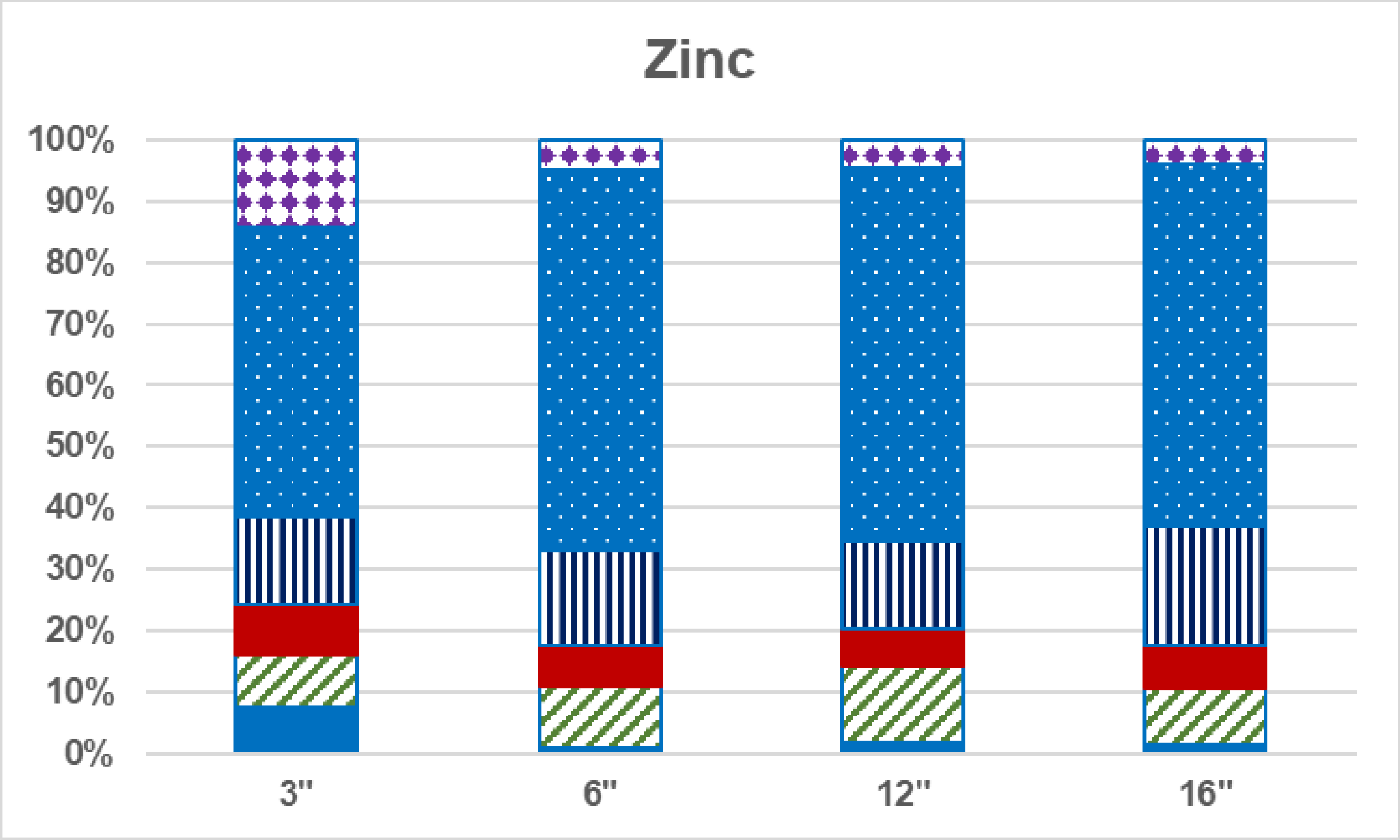

[redacted] [redacted] [redacted] [redacted]

- Water drawn down to just under surface
  - Allow samplers to walk to sampling locations
- Samples collected at 3”, 6”, 12”, and 16”
- Immediately placed in bag and vacuum sealed
  - Placed in second bag and vacuum sealed
- Placed on ice until delivered to lab
  - Stored at 4° C until analyzed

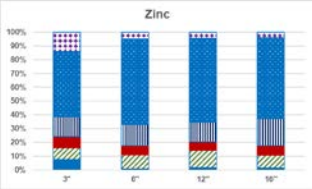
Sequential extractions

Fraction	Target	Reagents and procedure
Exchangeable	Metals that may be released through ion-exchange processes or are weakly adsorbed to the substrate surface	8-mL 1 M $MgCl_2$ at pH 7 Agitated for 1 hour
Bound to carbonate	Metals that are precipitated or co-precipitated with carbonate and metals that are adsorbed to carbonate surfaces	20-mL 1 M NaOAc adjusted to pH 5 with HOAc Agitated for 1 hour and repeated
Bound to labile organic matter	Metals that are bound in humic and fulvic acids through complexation	30-mL 0.1 M $Na_4P_2O_7 \cdot 10H_2O$ at pH 10 Agitated for 1 hour and repeated
Bound to Fe/Mn oxides	Fe and Mn oxides and any metals that may be adsorbed to them	20-mL of 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc Agitated for 1 hour
Bound to refractory organic matter and sulfides	Metals that are bound to sulfides and decay-resistant organic matter with low solubility	3-mL of 0.02 M HNO_3 and 5-mL 30% H_2O_2 adjusted to pH 2 with HNO_3 Heated to 85±2°C for 2 hours with occasional agitation 3-mL 30% H_2O_2 Heated to 85±2°C for 3 more hours with occasional agitation After cooling, 5-mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 and 4-mL sparged ultrapure water Agitated for 30 min
Residual	Metals that are bound to primary and secondary minerals, particularly silicates, which typically enter the environment through weathering	10-mL concentrated HNO_3 Microwave digestion

Results and Conclusions

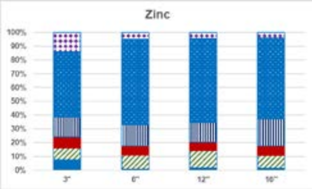


Water quality improvements

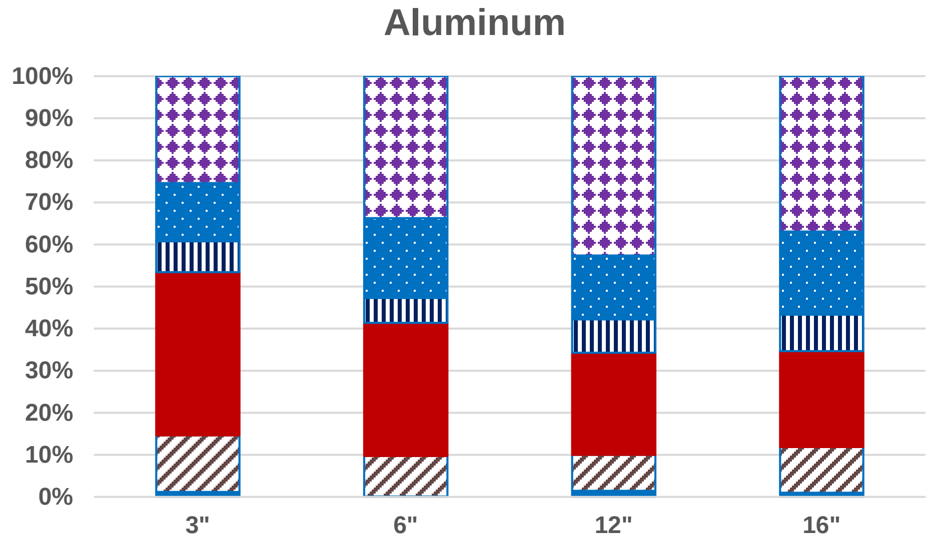


	IN	OUT
Flow (L/min) (gpm)	9 (2.35)	9 (2.35)
Temperature	18.8 ± 2.4	19.1 ± 4.2
pH	3.3 ± 0.6	6.3 ± 0.6
Specific Conductance	775 ± 400	1082 ± 430
ORP	221 ± 168	-115 ± 231
Al	19 ± 21	0.11 ± 0.18
Cu	0.17 ± 0.19	0.01 ± 0.002
Fe	82 ± 84	14 ± 27
Mn	2.6 ± 0.8	4.5 ± 2.6
Pb	0.11 ± 0.91	0.003 ± 0.005
Zn	1.2 ± 6.7	0.09 ± 0.56
Sulfate	470 ± 450	180 ± 250

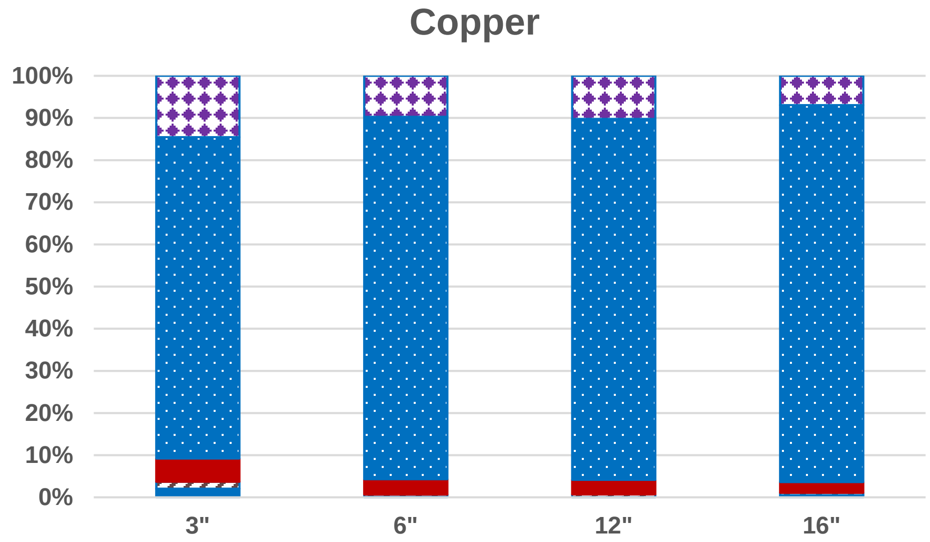
Total Metals



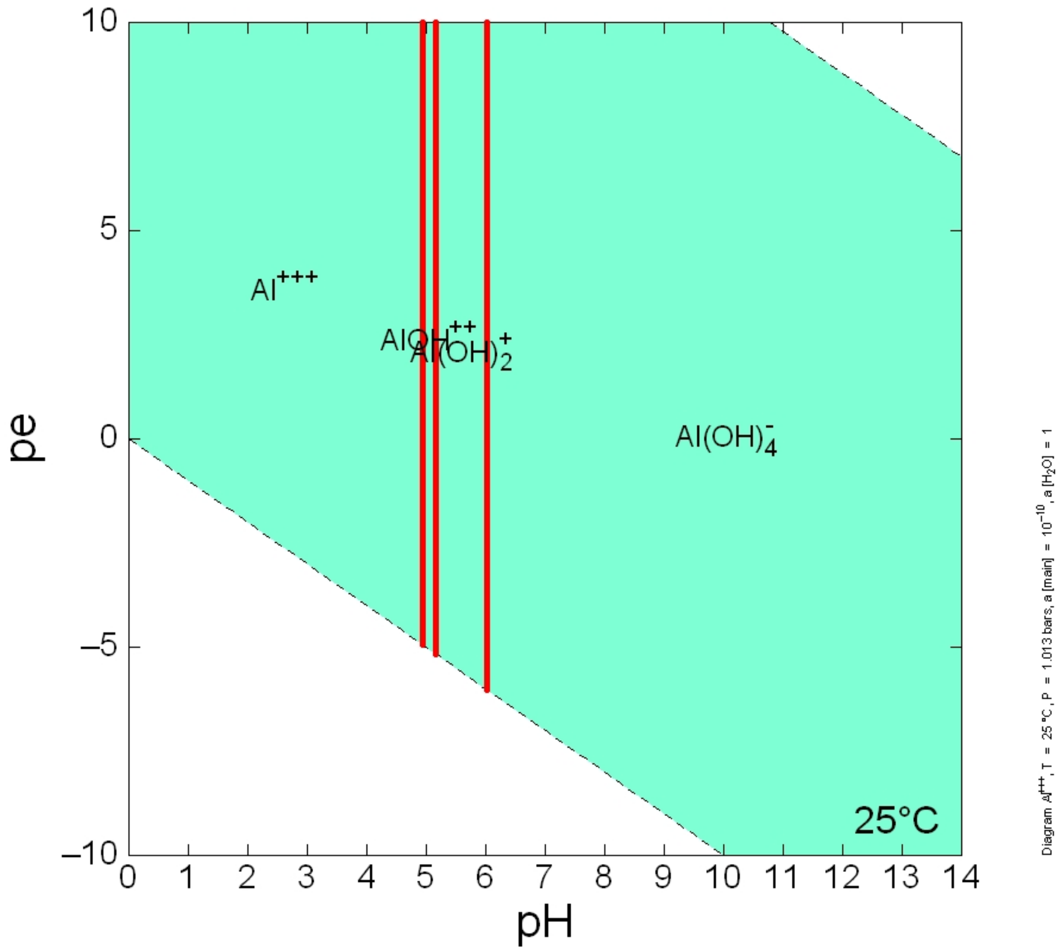
	3”	6”	12”	16”
Al	7670	3880	2310	2820
Cd	8	5	4	3
Co	34	92	74	26
Cr	17	18	15	13
Cu	88	190	83	60
Fe	101,000	38,500	11,400	10,500
Mn	440	420	420	410
Ni	65	25	70	33
Pb	60	38	28	27
Zn	330	490	720	560

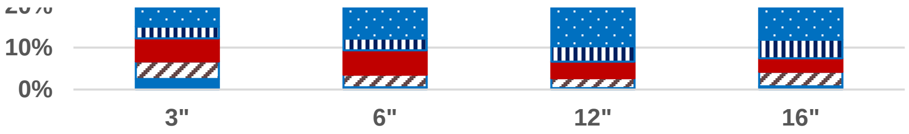


Aluminum



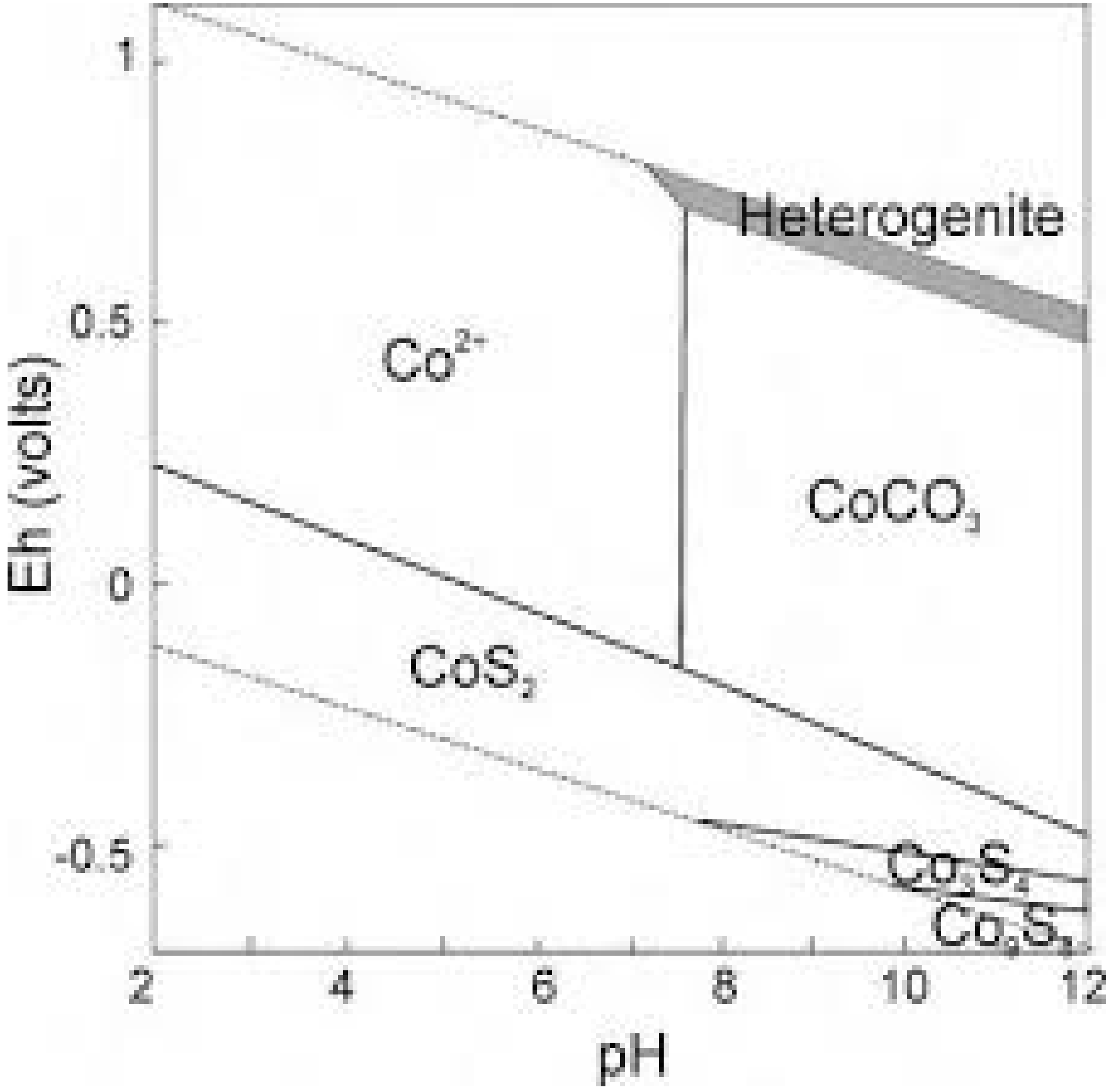
Copper

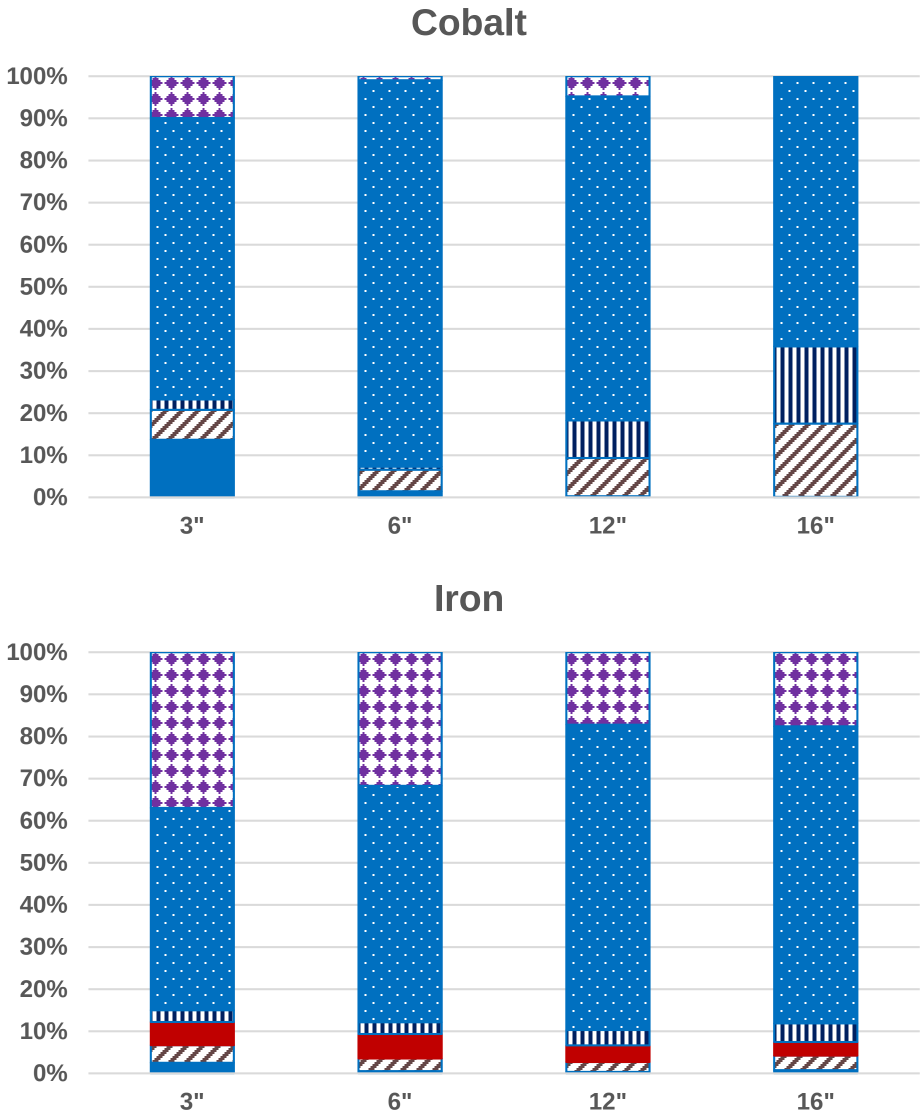




■ **Exchangeable** ▨ **Carbonate** ■ **Labile Organic**

▥ **Oxide** ■ **Refractory Organic/Sulfide** ▩ **Residual**





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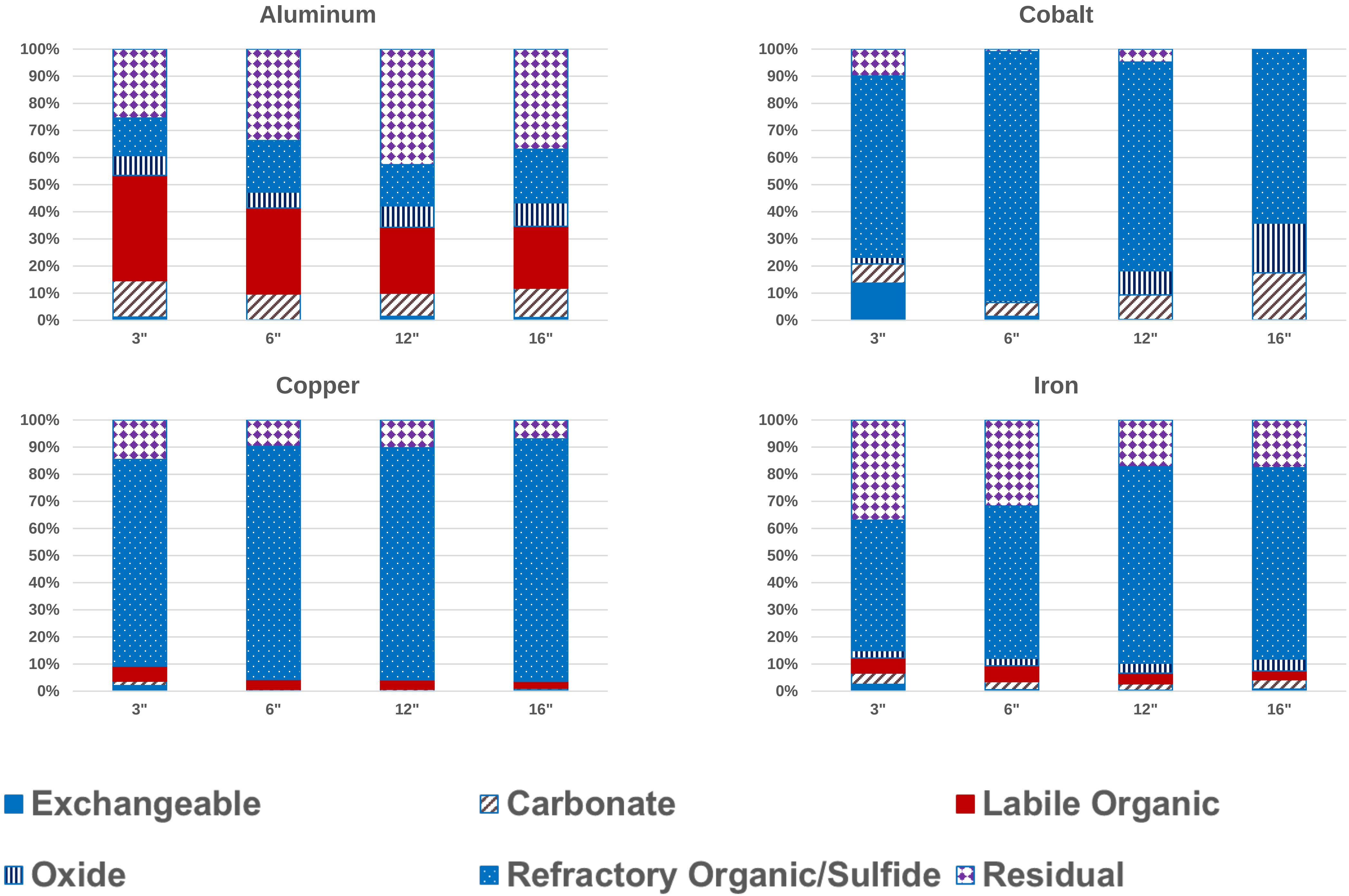
Aluminum
Cobalt
Copper
Iron
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
3"
6"
12"
16"
■ Exchangeable
▨ Carbonate
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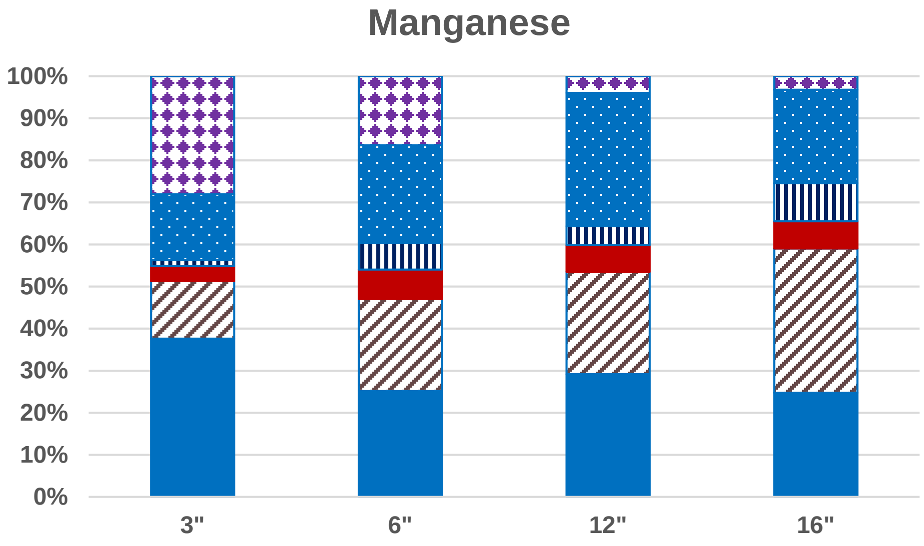

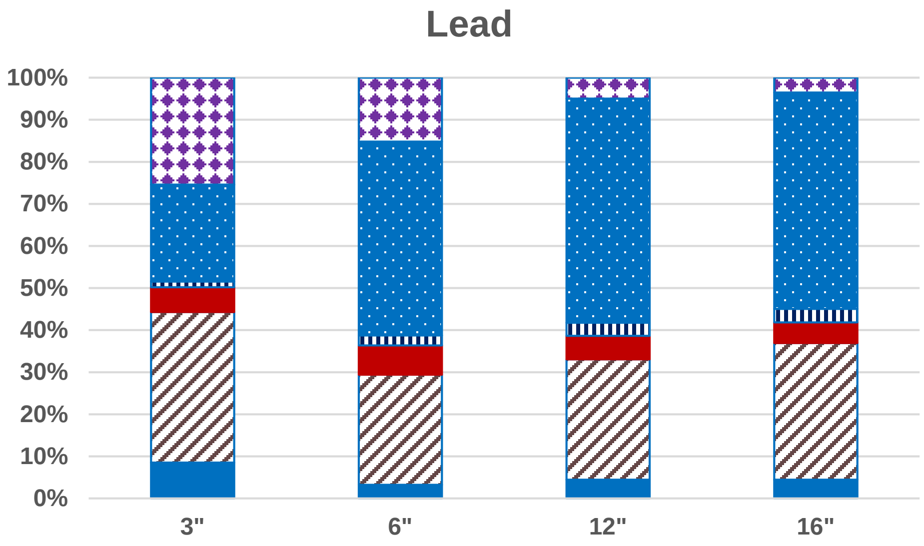

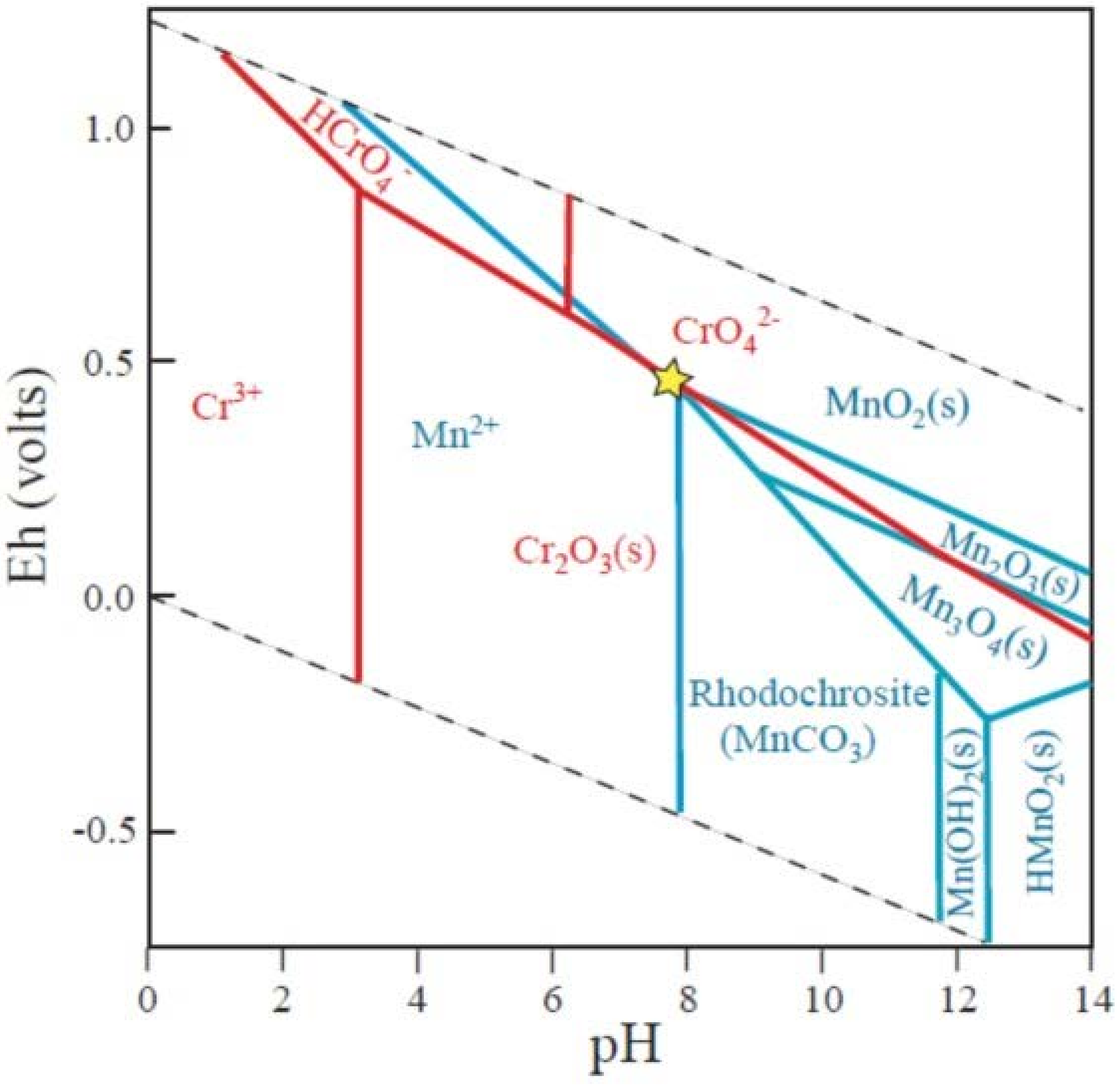

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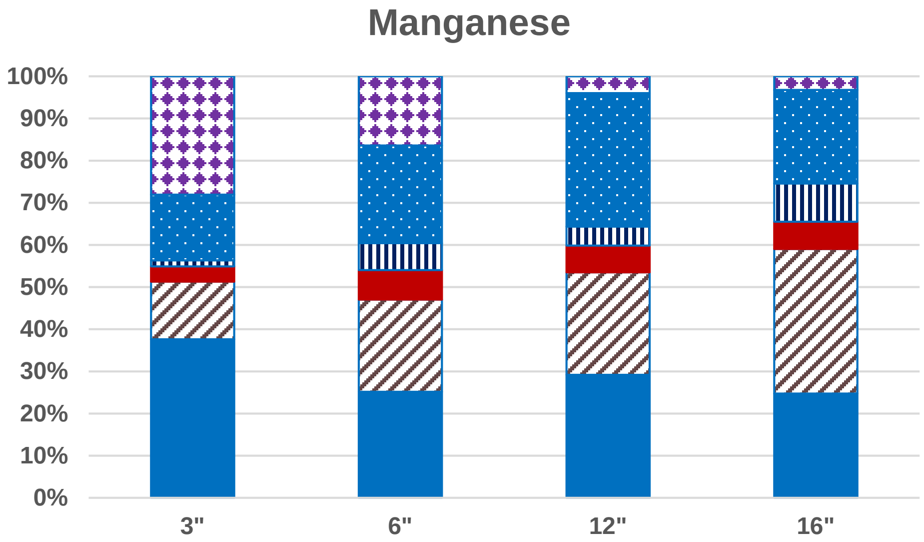

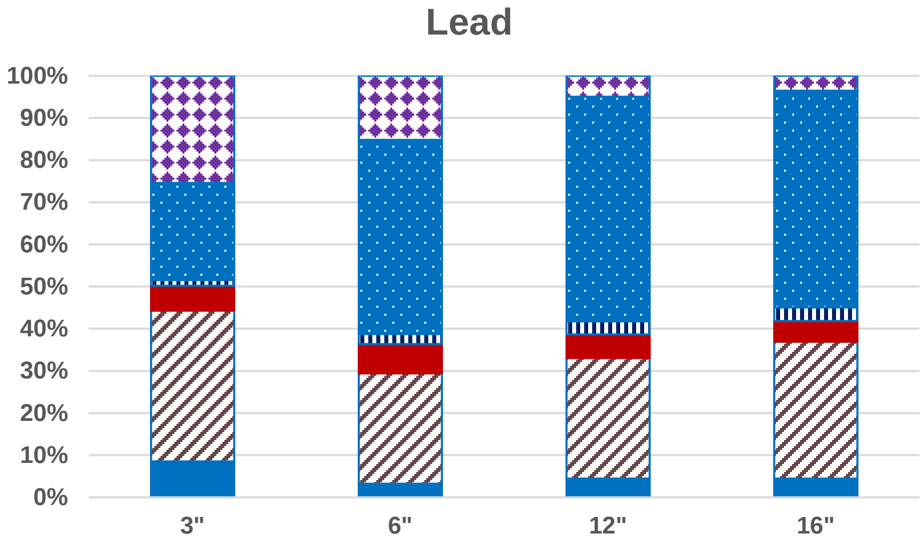

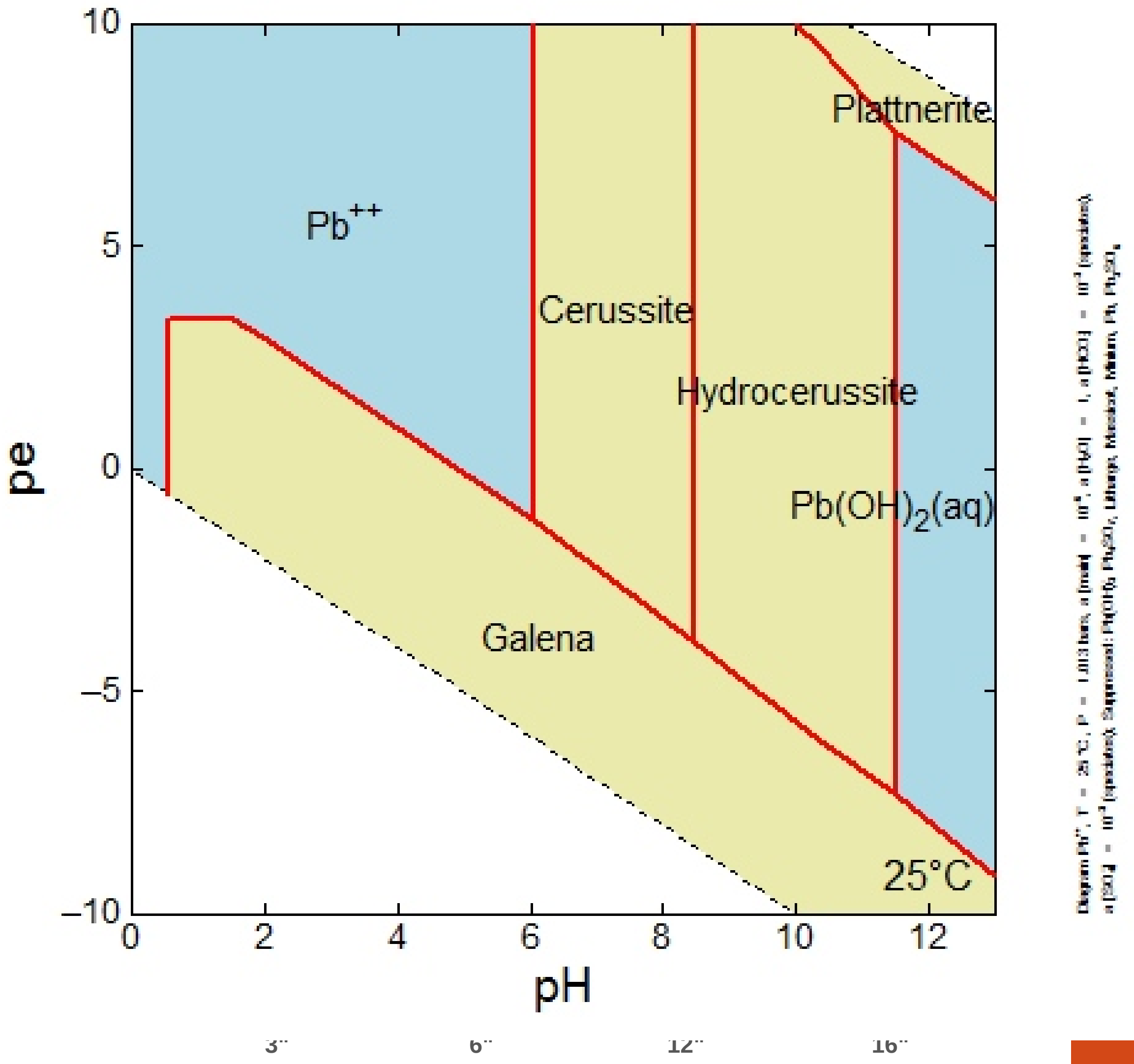

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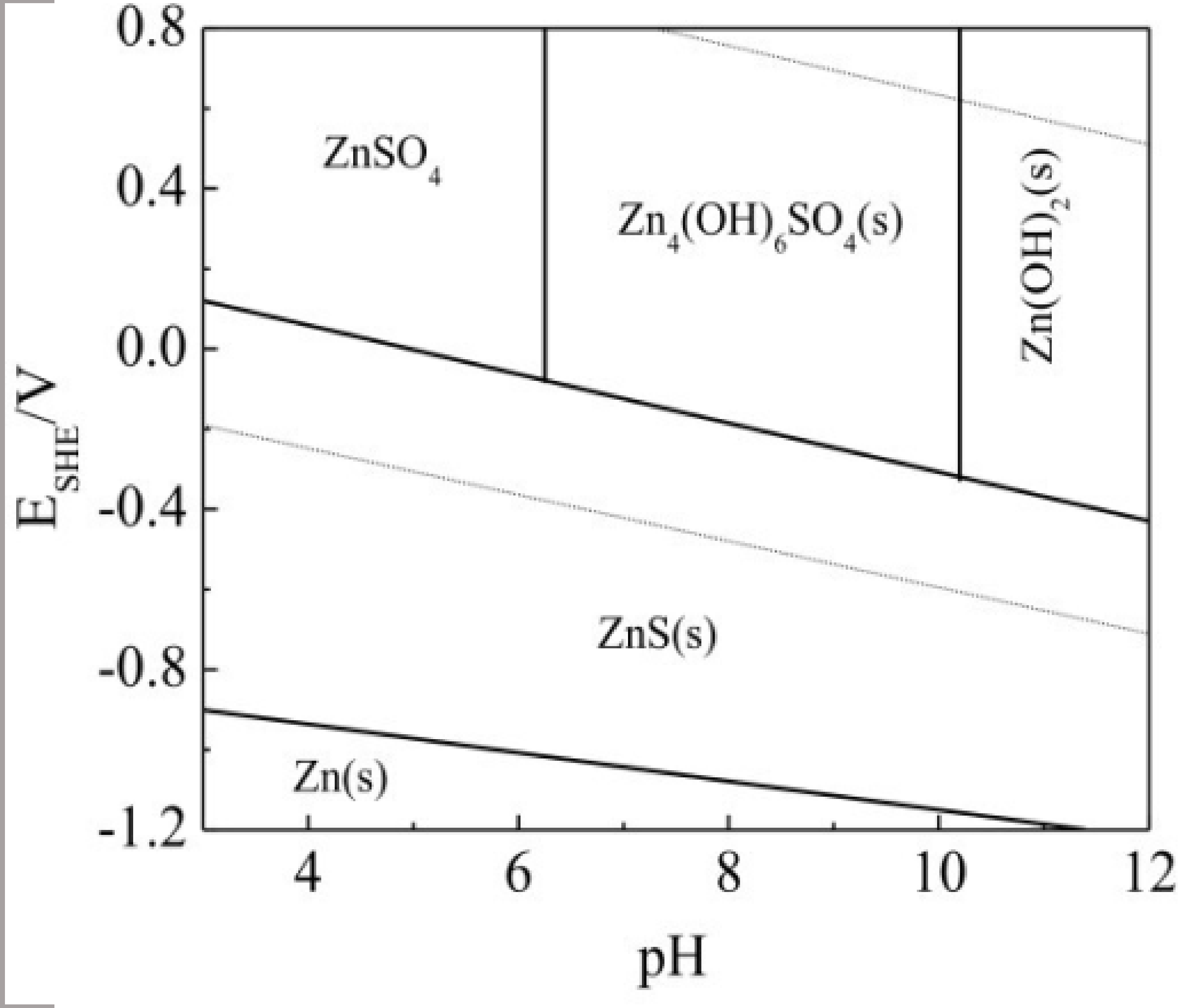

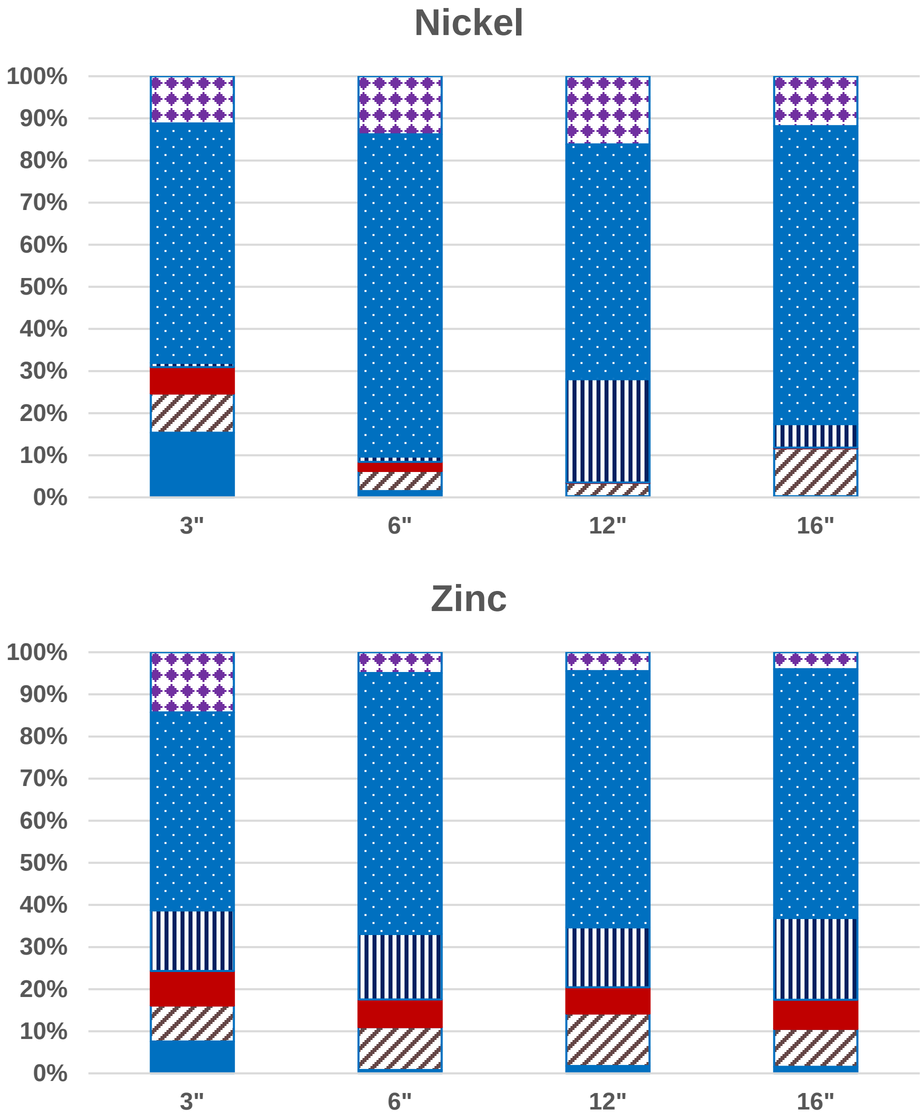

■ Exchangeable
▨ Carbonate
■ Labile Organic
▥ Oxide
■ Refractory Organic/Sulfide
▩ Residual

Conclusions

- Overall, majority of metals found in the stable, non-bioavailable sulfide fraction
  - Exceptions = Al and Mn
  - Fe was surprising, but likely dominated by well-formed oxides near the surface
- In general, percentages of metals found in carbonate or sulfide fractions increased with depth
  - Sometimes at the expense of each other
  - Sometimes at the expense of the residual fraction

Acknowledgements

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- Paul Eger
- OU CREW
- St. Francis University

QUESTIONS?