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Manganese recovery from ozone technology in mine water treatment

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Contributors

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Natural manganese occurrence

- Ranks about 12th in crustal abundance
- Of the heavy metals, surpassed only by iron
- Component of over 100 minerals
- Median concentrations of MnO in rocks of the Appalachian Pennsylvanian-age formations range from 0.04 to 0.09 % (XRF)
- Mn correlated with siderite in Appalachian rocks (over 2500 analyses of non-coal lithologies)
- Median concentration of MnO in Appalachian coals is 0.1% on an ash basis (18 ppm on whole-coal basis)

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Manganese uses

- Major use in iron and steel production (~85% of total US demand – almost all Mn imported); dry cell batteries, hybrid car batteries, matches, animal feed, bricks
- Mn is an essential nutrient, but does have a HRL of 0.3 mg/L

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Ozone reaction

$$3Mn^{2+} + O_3 + 3H_2O = 3MnO_2 + 6H^+$$

Gibbs free energy ΔG = -38.985 kcal at 10° C

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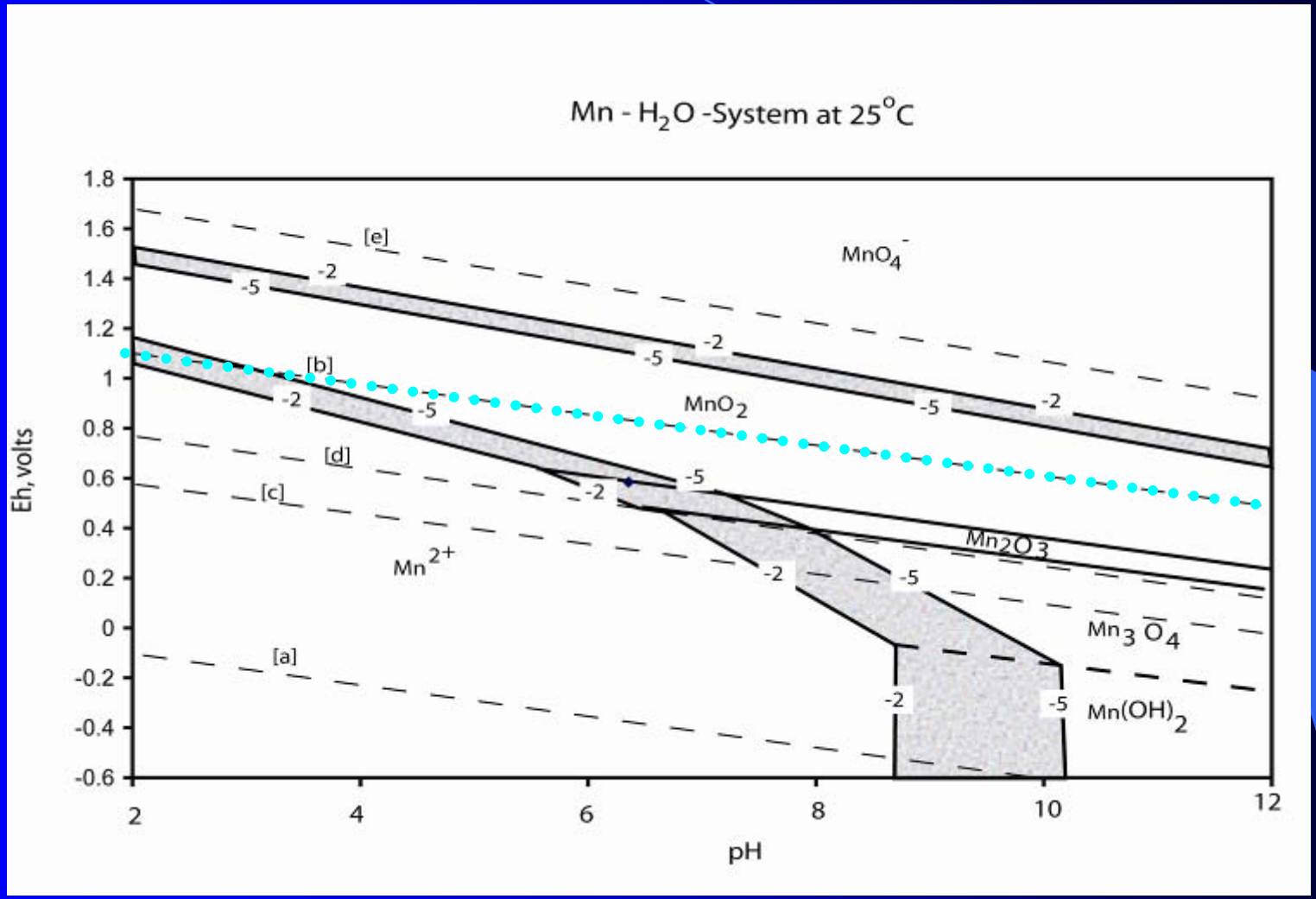
Manganese stability diagram



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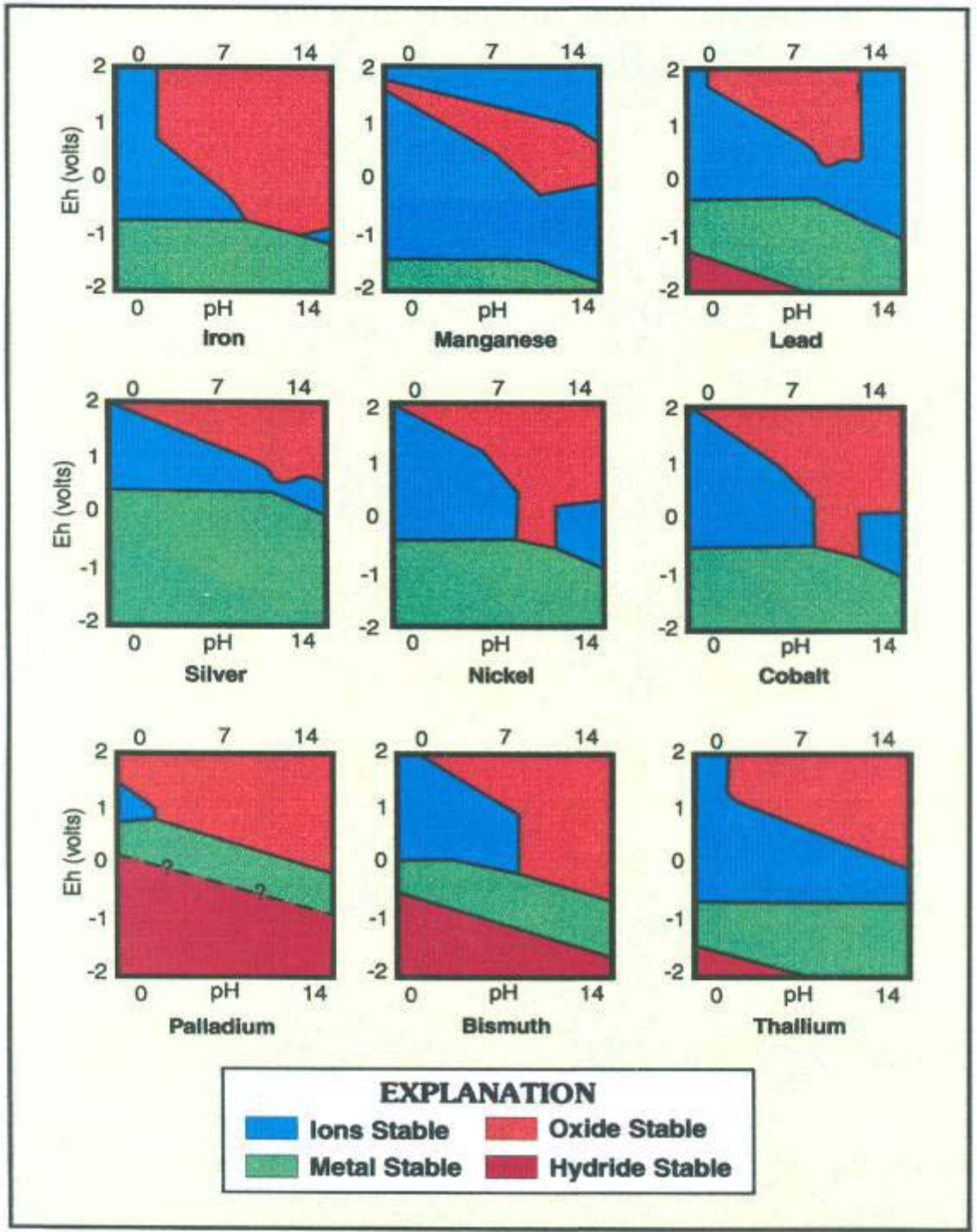
Metal stability field diagrams



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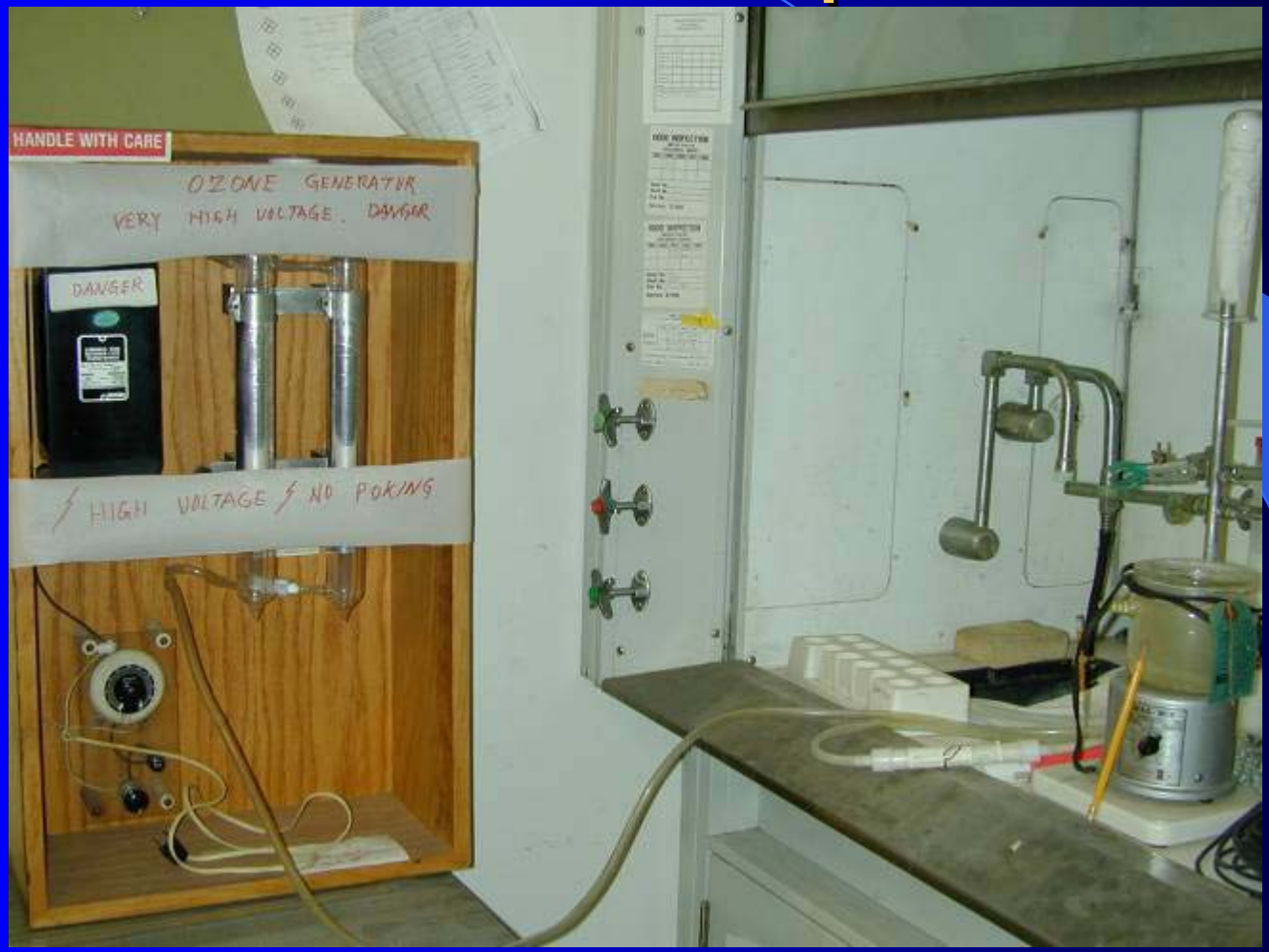
Bench-scale experiment



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Pennsylvania, U.S.A

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Limestone vats

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Water wheel

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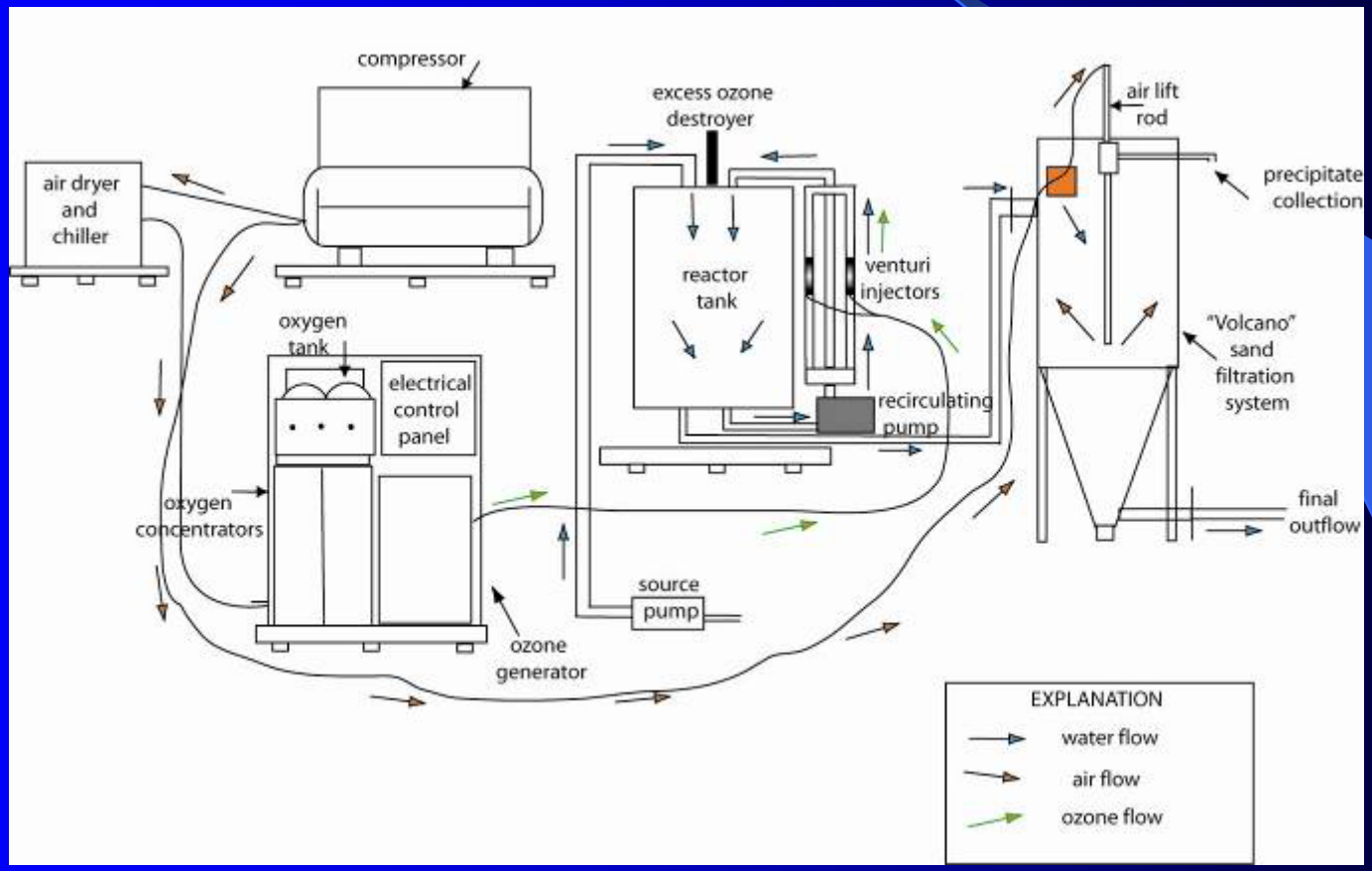
Schematic of pilot-scale ozonation system



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Ozonation remediation system

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Ozone generator

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ORP controller and sensor

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Venturi injectors

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Effluent into trench and Little Toby Creek

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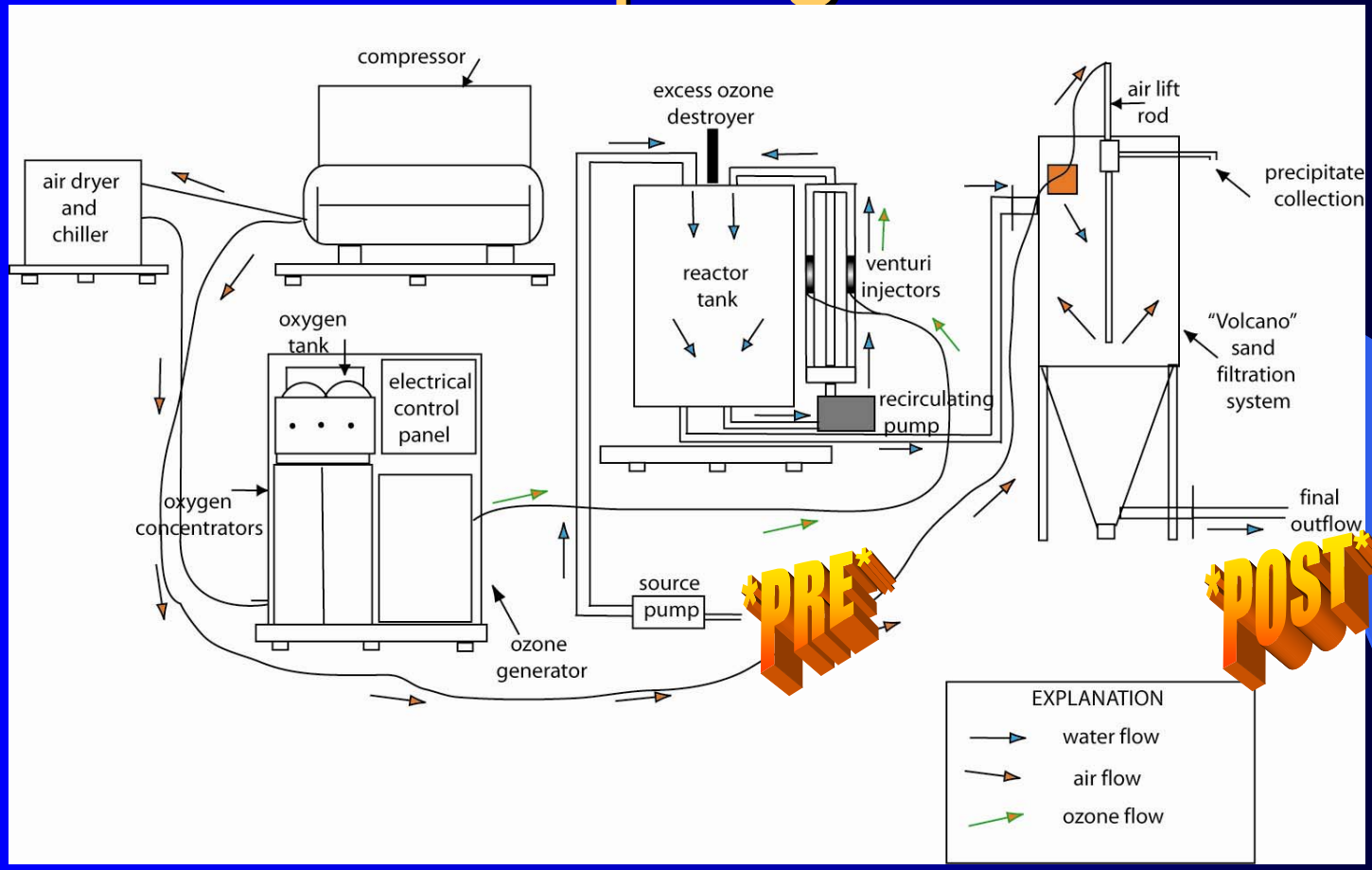
Water sampling locations



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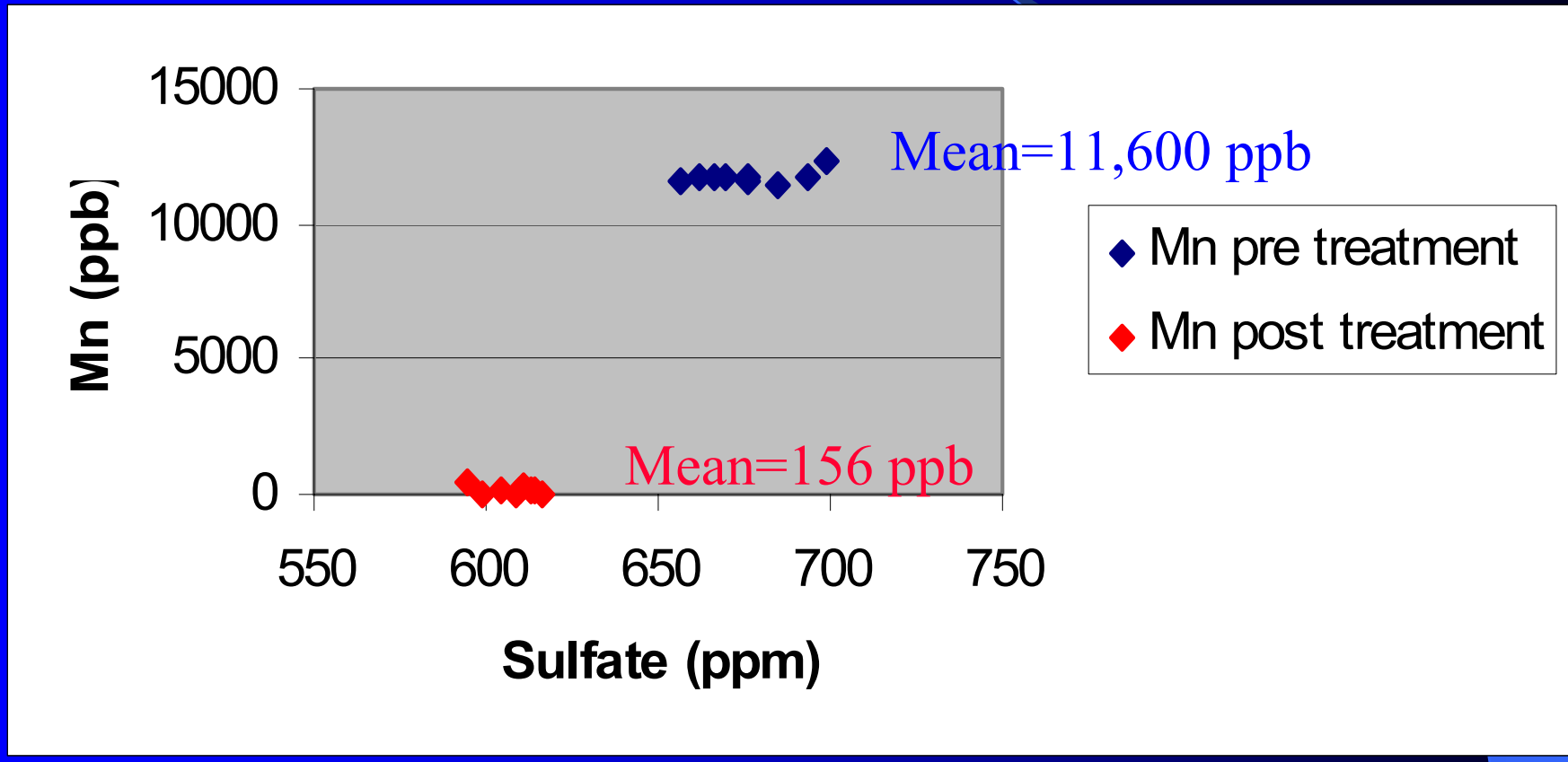
Dissolved Mn^{2+} concentrations



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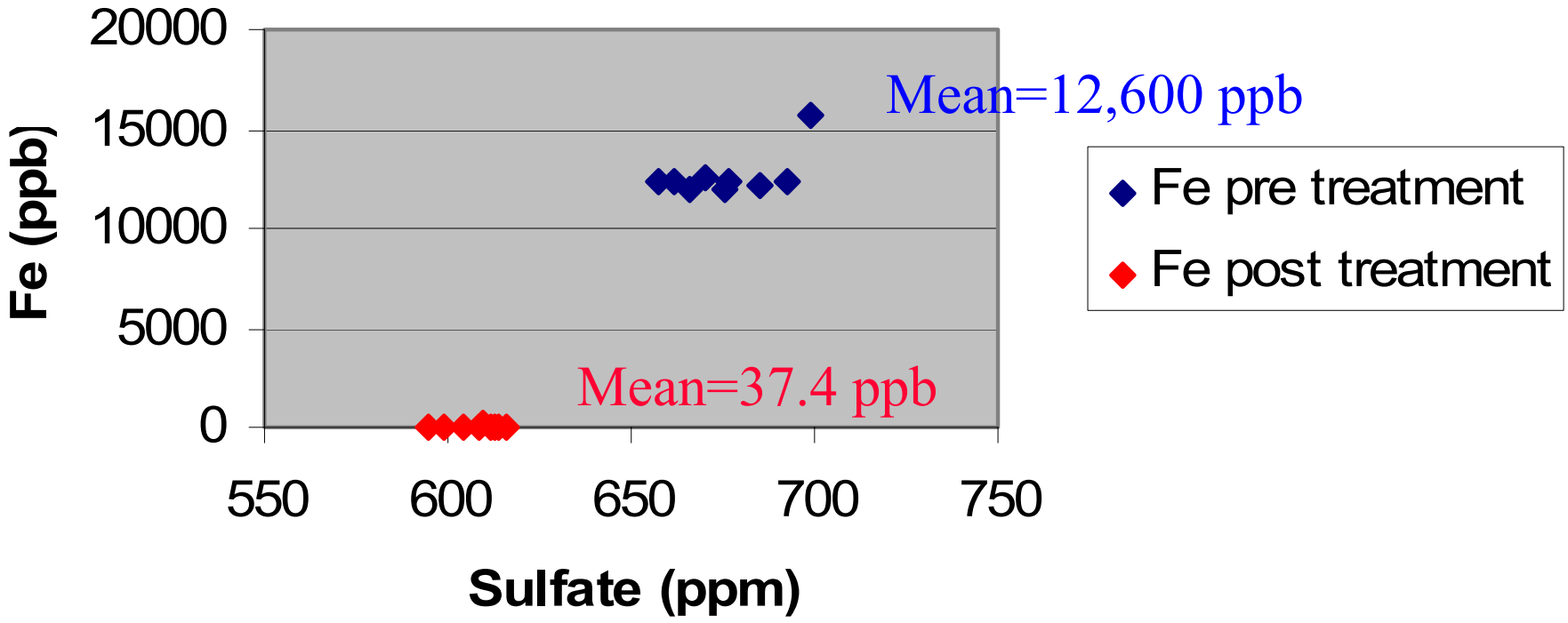
Dissolved Fe concentrations



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Decreases in means of other parameters

- Al 277 to 28 ppb 66%
- Co 32 to 7 ppb 78 %
- Ni 82 to 75 ppb 8%
- Pb 1 to 1 ppb 0%
- Ba 13 to 5 ppb 61%
- Zn 121 to 54 ppb 55%
- pH 6.1 to 6.1 0%
- Ag, Bi, Tl BDL

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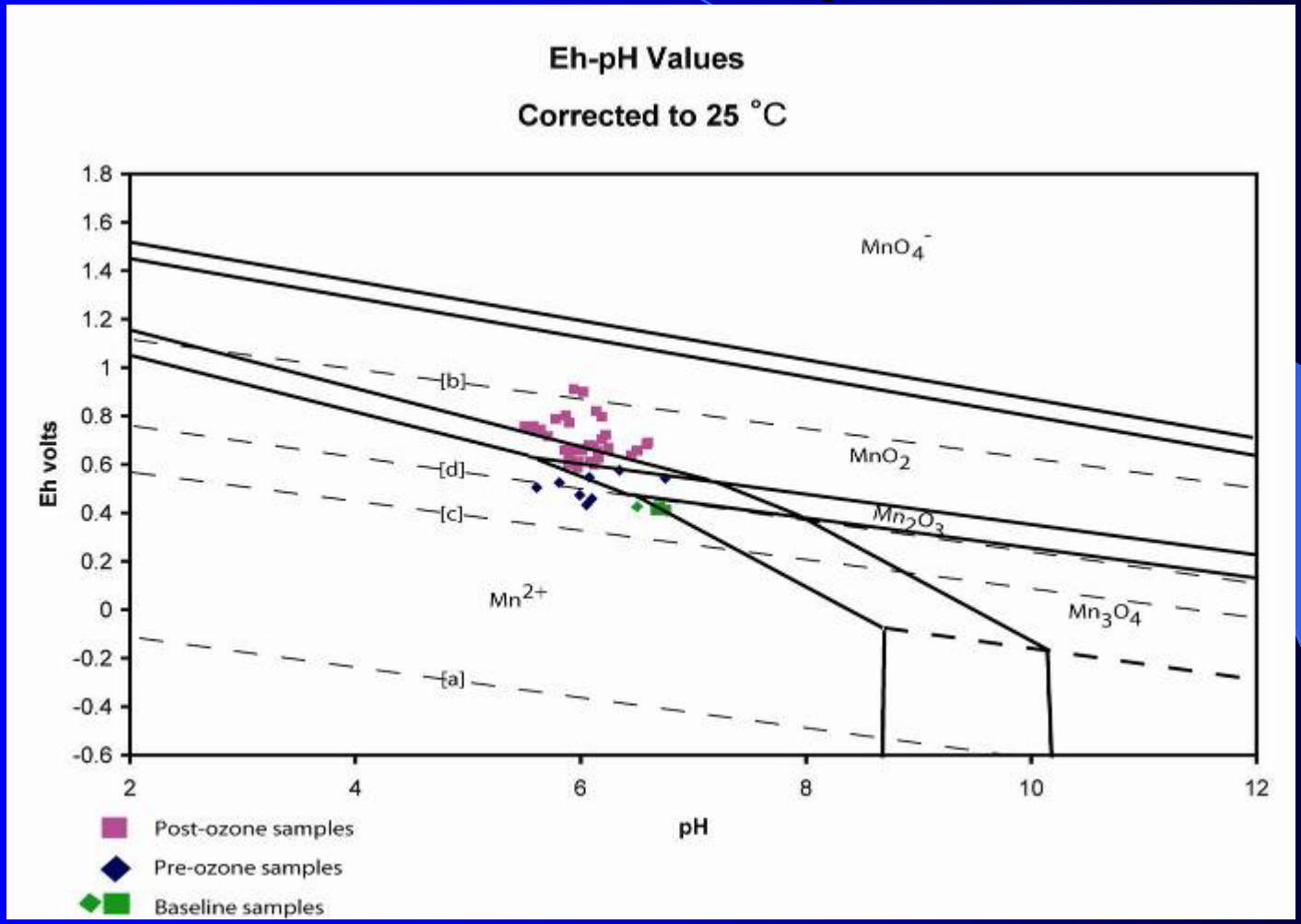
Water samples



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Collection trough

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Precipitate

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Dried precipitate

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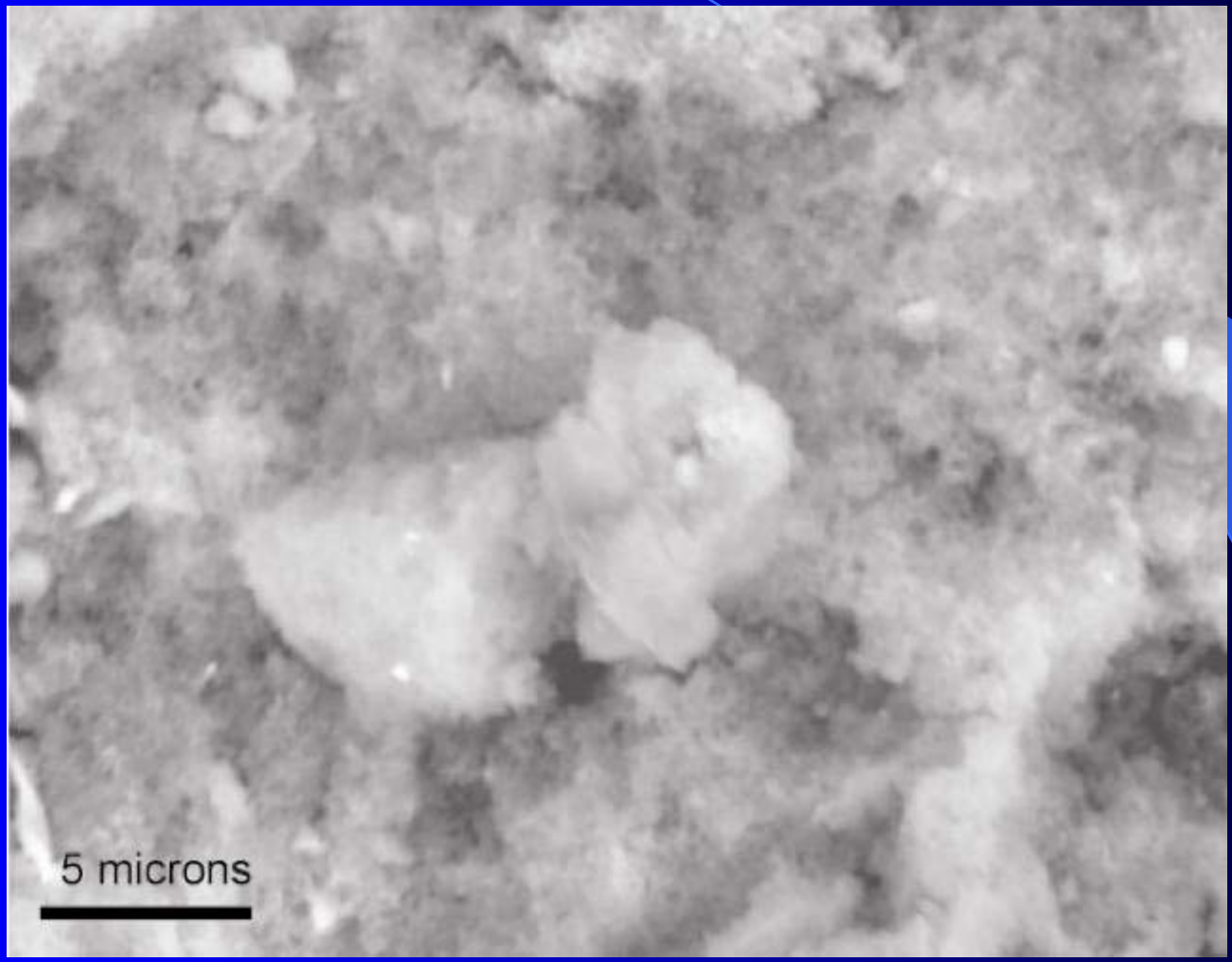
SEM photomicrograph



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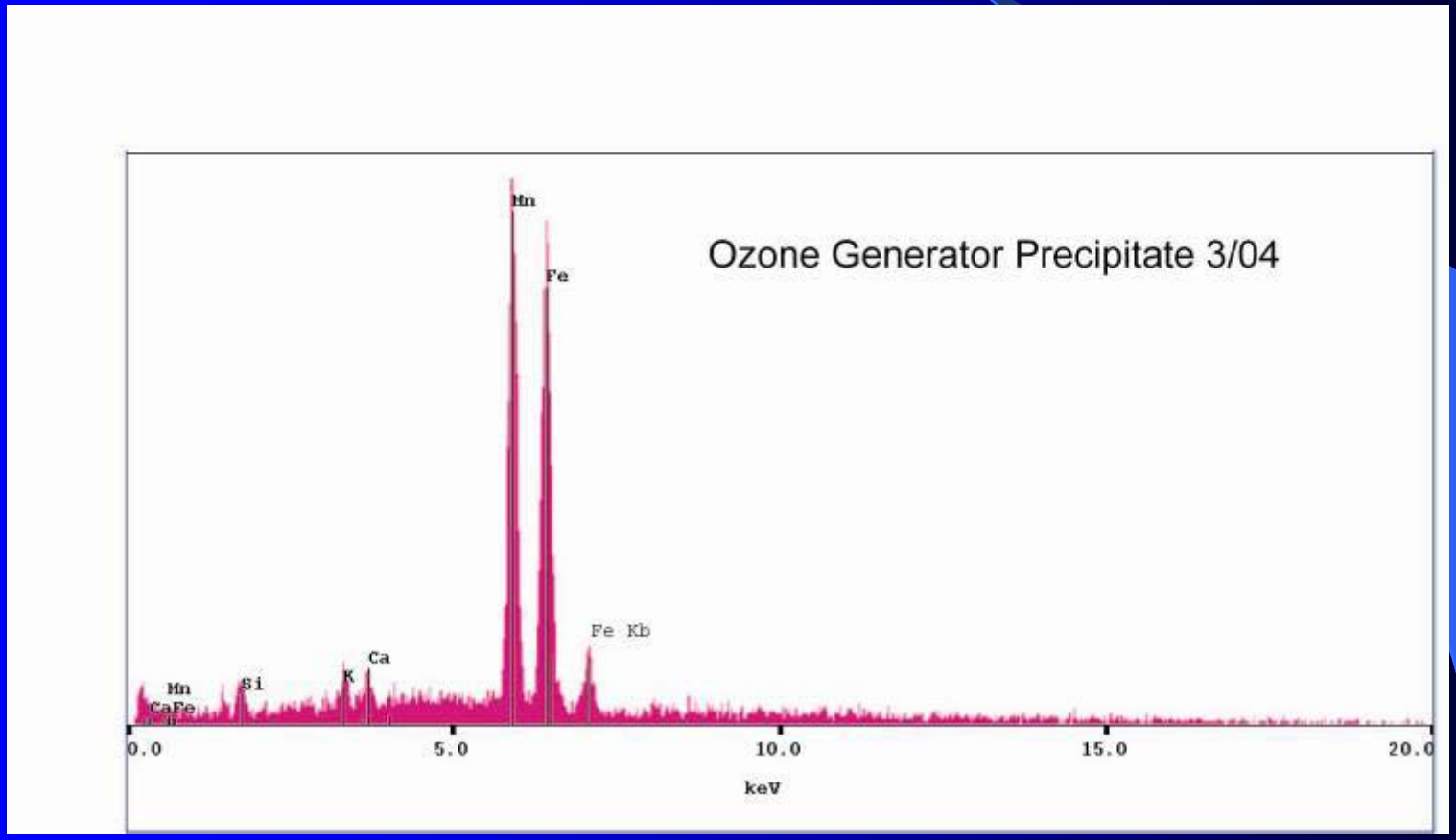
Energy Dispersive Xray



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New filter

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Treating raw drainage

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Raw water Fe/Mn precipitate

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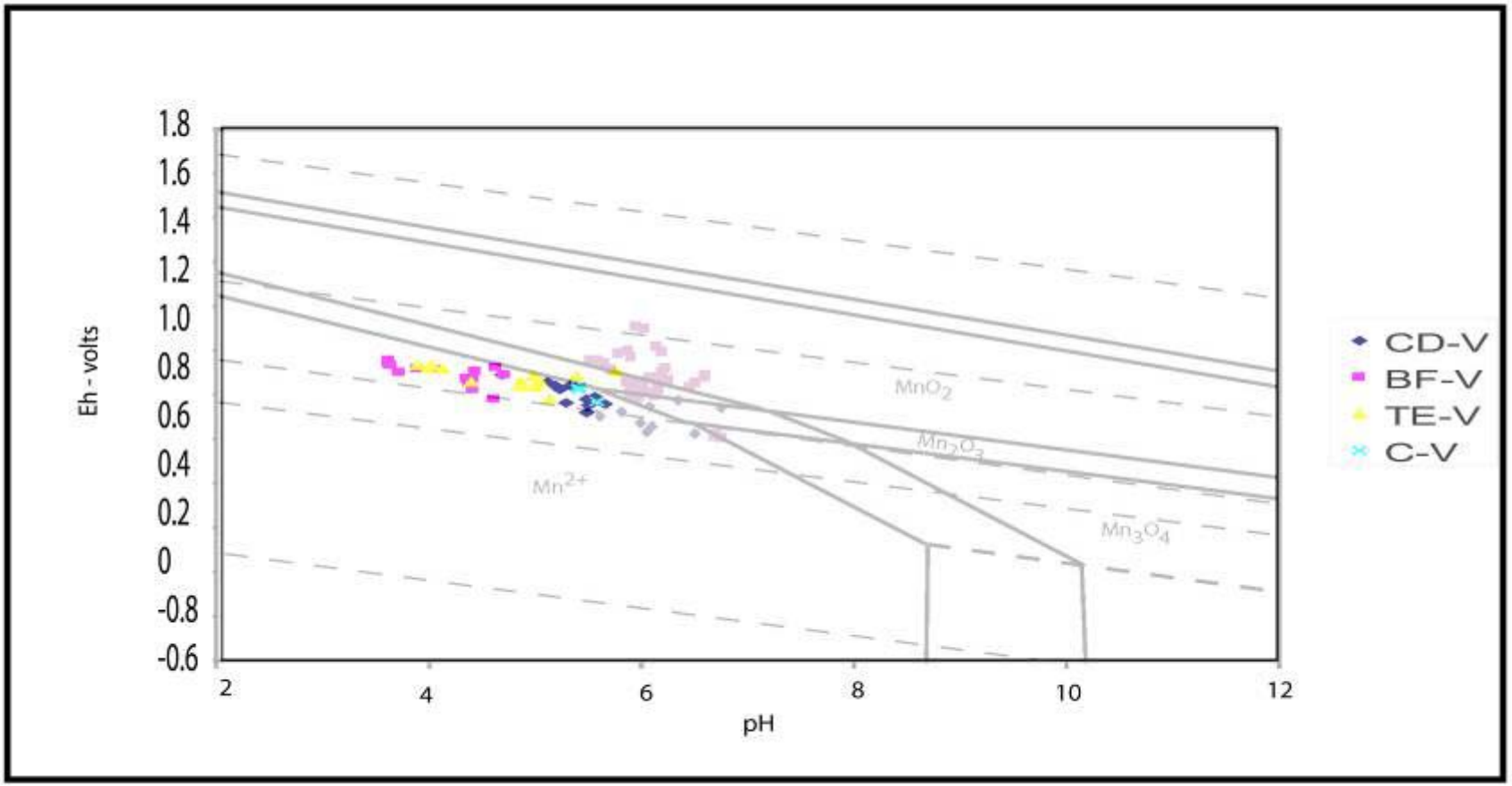
‘Raw’ water results



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Costs

- Capital investment
  - hardware $57, 300
- Shipping $6,500
- Installation/plumbing/wiring services $6,000
- Operation costs
  - 100 amps = 296000 KwH/year = $17,700 yr
  - Replacement parts

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Conclusions

- Ozone can successfully precipitate dissolved Mn and Fe at the pilot scale
- Capture of fine-grained precipitate requires improvement
- Marketing analysis being done; further runs required to determine economics
- Implementation at another site desired

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