SUCCESSFUL CHEMICAL OXIDATION TREATMENT OF SULFOLANE

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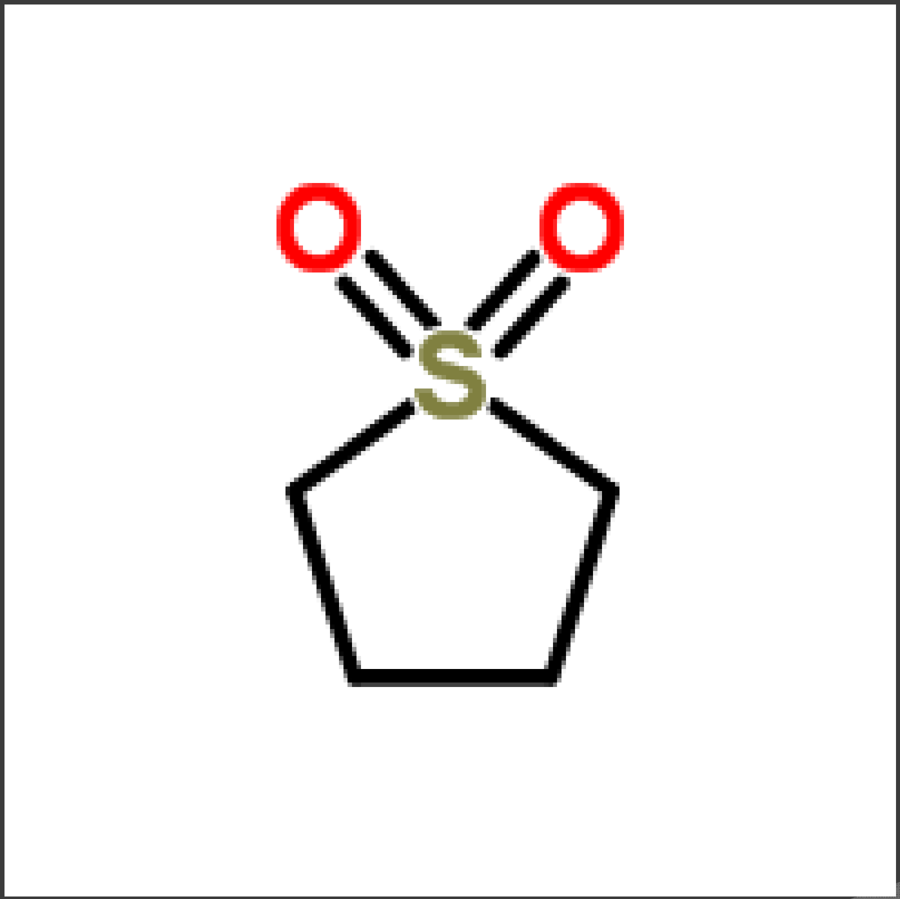
What is Sulfolane

- Manufactured for use in petroleum processing (aromatics extraction, sour gas sweetening).
- Highly soluble in water, has a high boiling point, and low vapor pressure and Henry's law constant.
- Does not volatilize from soil or water.
- Does not adsorb or attenuate in soil or saturated matrix.
- Moves with groundwater.
- Relatively stable in the environment.

For the more Technical Folks
It is Pentagon with two Passages



(Not funny.....mumbles the chemist)

What are the Issues?

- Sulfolane has been widely released into the environment.
- Under the radar because it is not routinely analyzed.
- Very few laboratories analyze for it.
- Toxicity data are evolving. EPA issued non-carcinogenic reference dose data in 2012. Texas has cleanup standards.
- Cleanup levels using EPA data and RA methodology are low.
- Little information on viable approaches to remediation.
- Wide distribution and low cleanup levels add a level of complexity to practicable remediation.

Technical Evaluation

- Former specialty chemicals plant
- Coastal zone
- Sulfolane in surface soil and groundwater.
- Groundwater in more permeable paleo-channels under the site.
- Sulfolane co-mingled with BTEX and TPH
- Customer preference for in-situ remediation over ex-situ options

Step 1

- Identify candidate technologies to treat sulfolane, BTEX, and TPH in groundwater.
- Evaluate the site data and obtain groundwater and soil for bench testing the candidate technologies.

Evaluation of Remedial Options

- Remedial options for BTEX and TPH are well developed, so the focus was on sulfolane
- Pump & treat
  - On-going at a site in Alaska
  - High sustained capital investment
  - Sulfolane drives complexity of water treatment process
  - Disposal of produced water
  - Long time frame to reach cleanup
- Biological
  - Low initial capital cost
  - Difficult to mimic laboratory conditions in the field
  - Long time frame to reach sulfolane cleanup
- In-situ Chemical Oxidation
  - Known to be effective for BTEX and TPH.
  - Medium capital and O&M costs[w3]
  - Medium time-frame, rebound and re-treatment usually required.

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w3 Typically no O&M costs only monitoring
wmoody, 11/7/2013

Evaluation of Remedial Options

- In-Situ Chemical Oxidation selected technology for bench testing.
  - Activated Sodium Persulfate (ASP)
    - Aggressive oxidant, but no heat or offgases.
    - Moderate lifetime (weeks).
    - High oxidant and activator costs (formula weight 238 g/mol vs 34 g/mol or seven times more persulfate).
  - Catalyzed Hydrogen Peroxide (CHP)
    - Aggressive oxidant with heat (controllable) and offgases (distribution, mixing, circulation, etc.)
    - Short lifetime (days) unless stabilizer is utilized.
    - Overall ower cost.
- CHP bench testing results are discussed in the following exhibits.

Catalyzed Hydrogen Peroxide

Primary reaction:

$H_2O_2 + Fe^{+2} \rightarrow OH\cdot + OH^- + Fe^{+3}$

$OH\cdot + \text{Organic Contaminant} \rightarrow CO_2 + H_2O$

Other reactions:

$OH\cdot + Fe^{+2} \rightarrow OH^- + Fe^{+3}$

$Fe^{+3} + H_2O_2 \rightarrow H^+ + HO_2\cdot + Fe^{+2}$

$Fe^{+2} + HO_2\cdot \rightarrow Fe^{+3} + HO_2^-$

$Fe^{+3} + HO_2\cdot \rightarrow Fe^{+2} + O_2 + H^+$

$OH\cdot + H_2O_2 \rightarrow H_2O + O_2\cdot^- + 2H^+$

$HO_2\cdot \rightarrow H^+ + O_2\cdot^-$

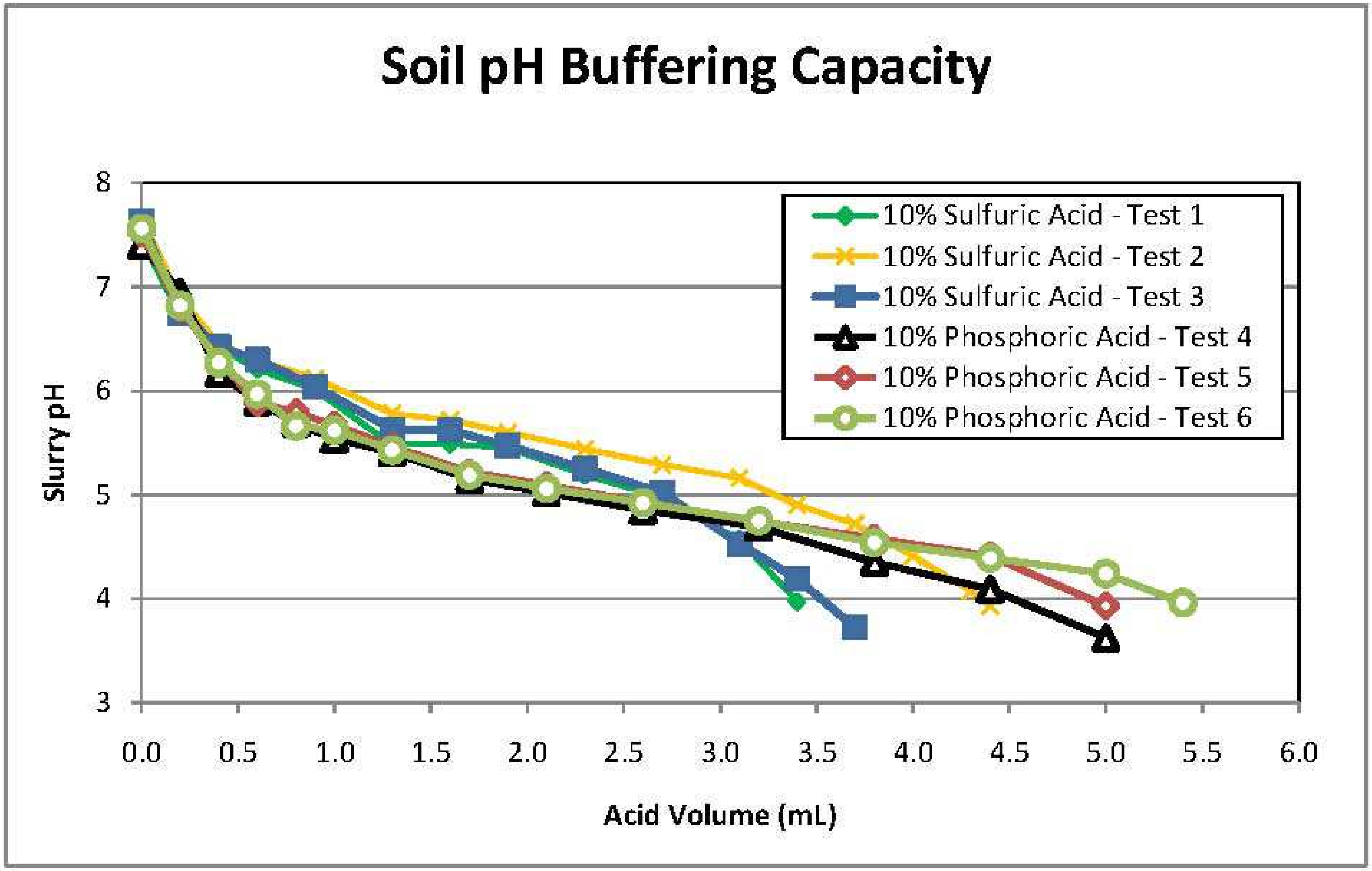
Bench Testing

- Baseline groundwater sampling
- Aquifer matrix testing (geochemical, pH, oxidant demand, buffering capacity)
- Reactor treatability testing
  - Aquifer matrix and groundwater from site well used for the slurry reactors
  - Tested a range of oxidant loading based on contaminant mass and experience
- Post-treatment groundwater sampling

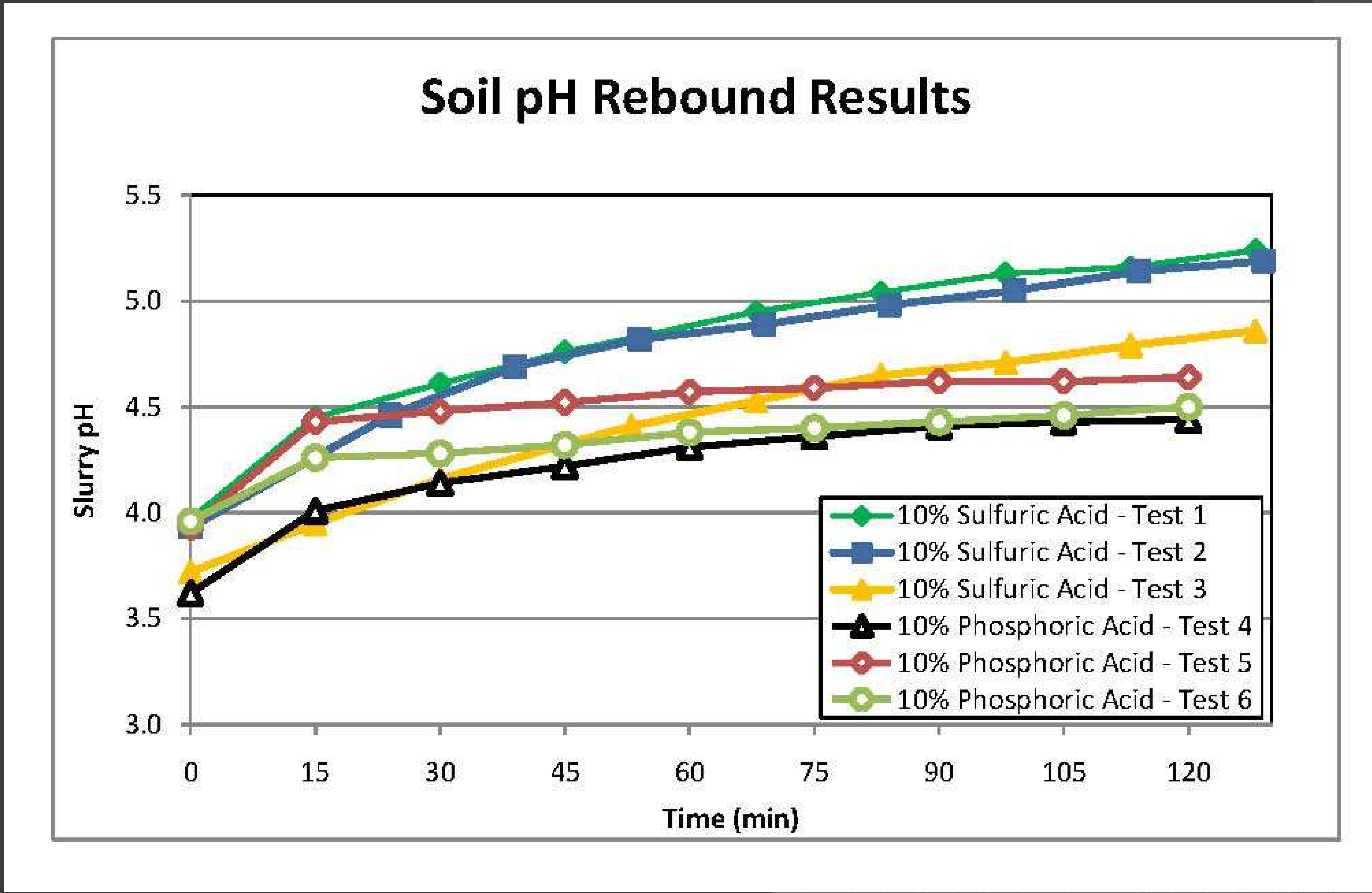
Contaminants and Test Setup

- Sulfolane at 2,800 ug/L in baseline water
- Low concentrations of VOCs
- Five sets of slurry reactors with different CHP dosages initiated and sampled after one week

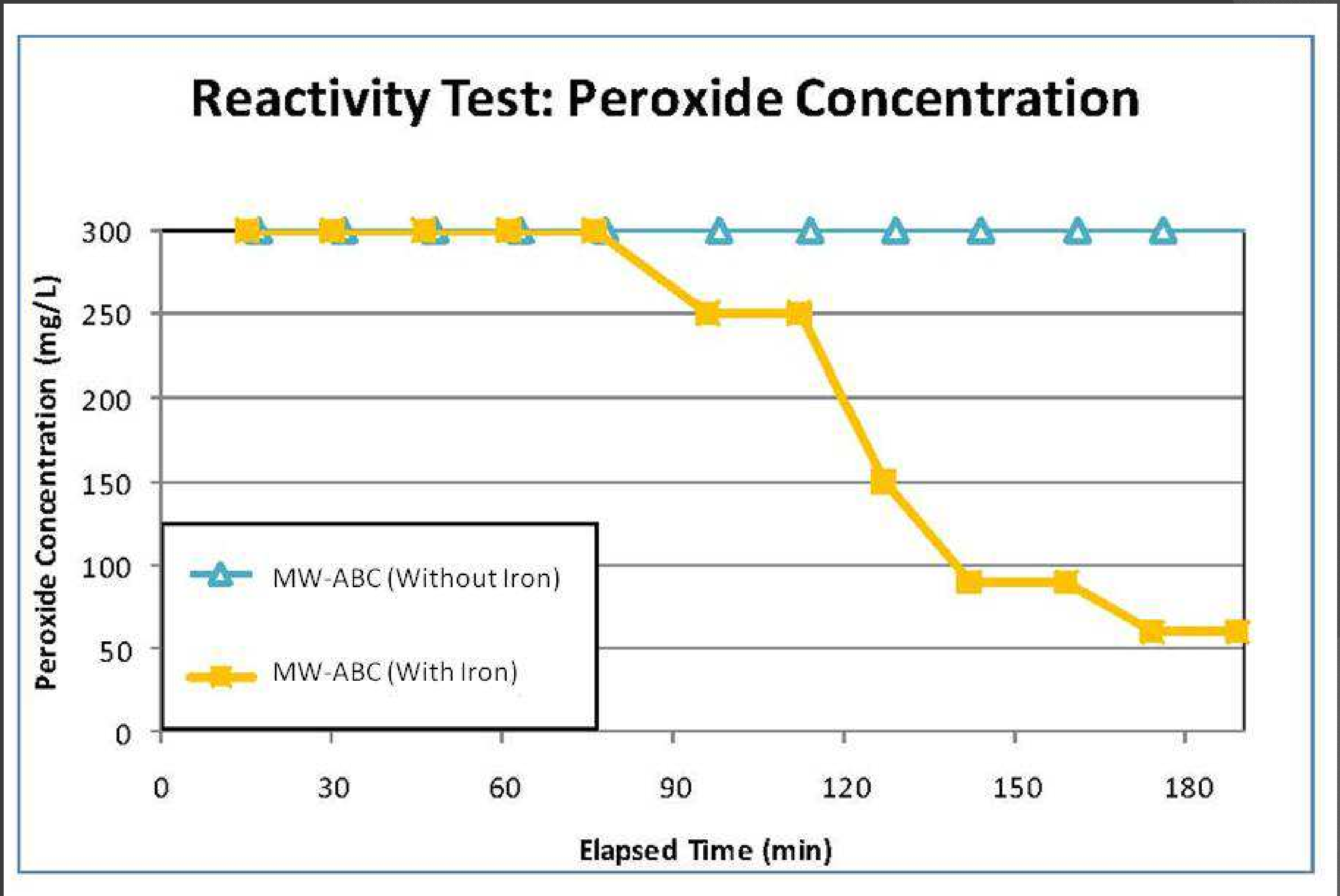
Buffering Capacity Results



Buffering Rebound Results

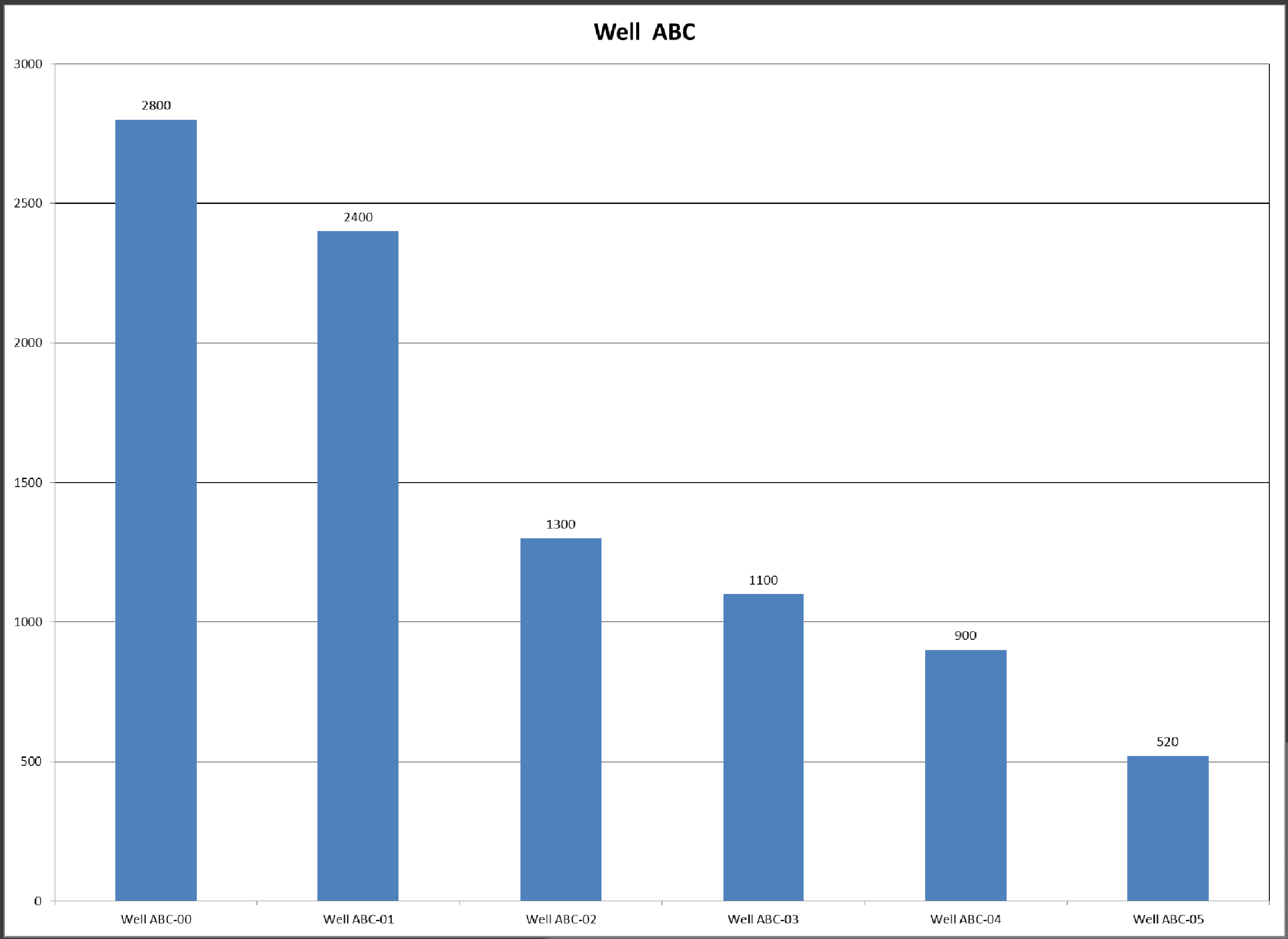


Reactivity Results



Treatability Results

Sulfolane (ug/L)

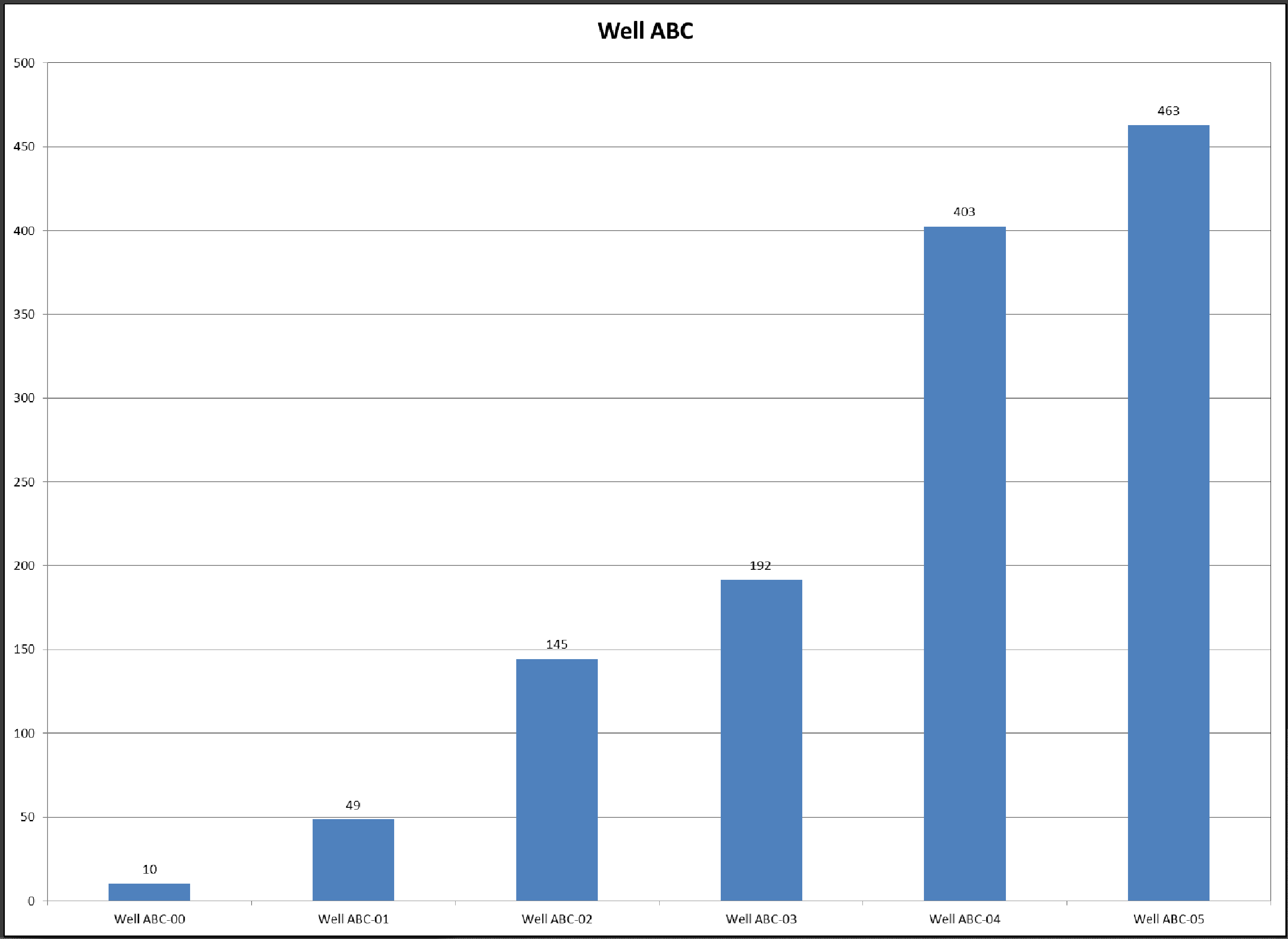


Key Conclusions

- Native soil had moderate to low pH buffering capacity
- Sulfolane mass was reduced linearly as a function of peroxide dosage
- ~70% reduction of sulfolane in dose 5
- Acetone byproduct was expected.
  - Common with most oxidant systems.
  - Naturally degrades.
- Metals concentration increase was expected.
  - Acidic CHP system utilized and positive ORP.
  - Metals will precipitate and conditions will return to pre-injection conditions

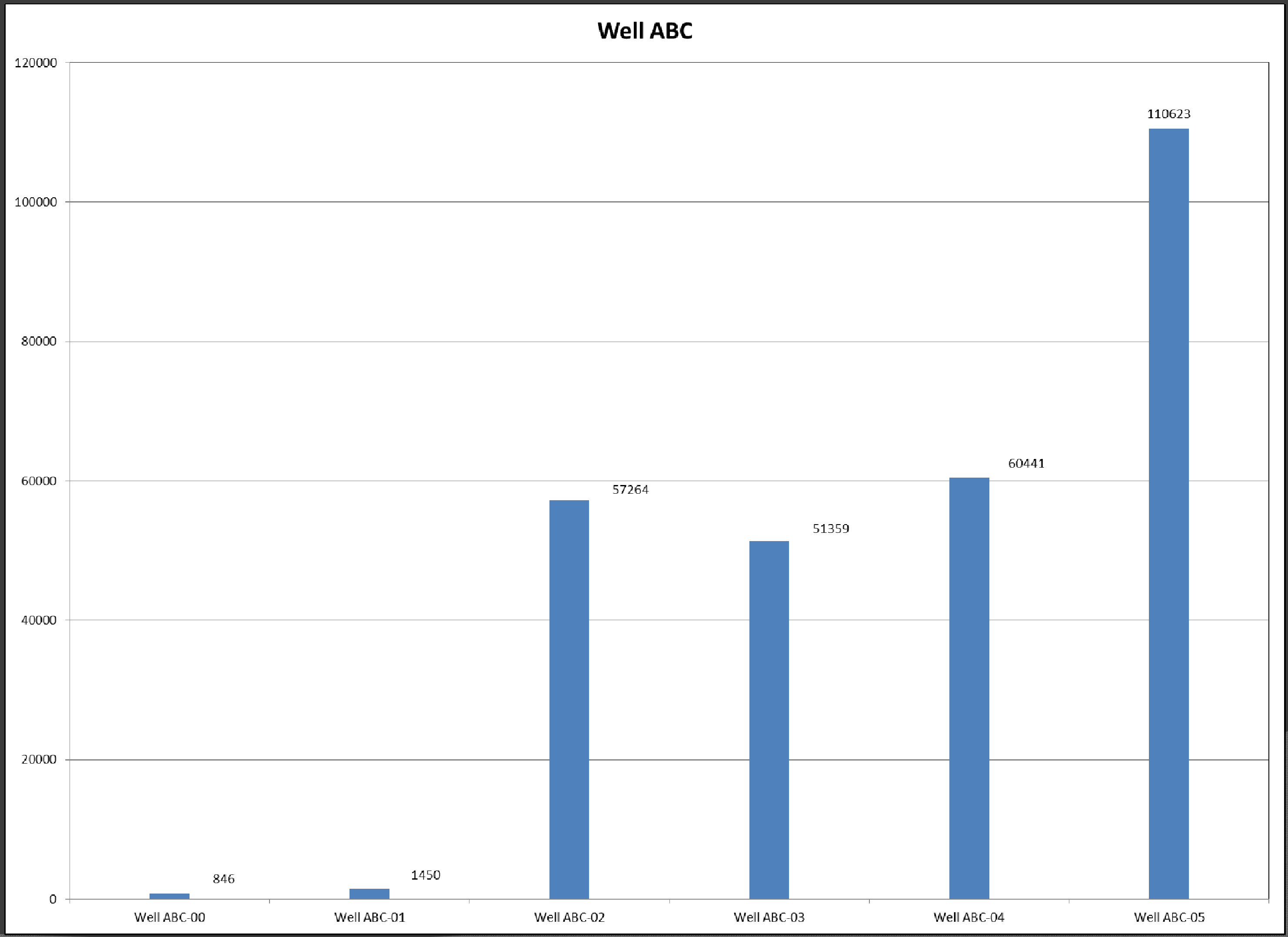
Treatability Results

Acetone (ug/L)



Treatability Results

Manganese (ug/L)



Next Steps

- Continuing work
  - Field-scale testing
  - Evaluate the extent of sulfolane destruction
- Questions?