MULTIPLE OXIDANT CHROMIUM LEACHING FROM HANFORD WASTE

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CHROMIUM PRECIPITATION LIMITS HIGH LEVEL WASTE (HLW) GLASS PROCESSING IN THE HANFORD WASTE TREATMENT PLANT (WTP) FLOWSHEET

- Cr loaded into glass above a certain limit (suggested 1.4%, Hrma et al.) precipitates as
  - spinel sludge ($[Fe,Ni,Mn][Cr,Fe]_2O_4$)
  - eskolaite (Cr_2O_3)
- Possible unwanted effects in the vitrification process and glass product:
  - Shorting of melter
  - Clogging melter pour spout

- Chromium has been limited to 0.5% wt in HLW glass to reduce processing time and number of high activity waste canisters produced by WTP

Photos: J.D. Vienna, Pacific Northwest National Laboratory

Eskolaite in Glass 0.010 mm

BASELINE PERMANGANTE LEACH

Selectively oxidatively leaches chromium from several different tank wastes (Rapko et al., 2004) with some Pu dissolution (OH^- dependent)

$Cr(OH)_3 + MnO_4^- + OH^- \leftrightarrow CrO_4^{2-} + MnO_2\downarrow + 2H_2O$ $\quad E = 0.588$

$8\ Cr(OH)_3 + 6\ MnO_4^- + 10\ OH^- \leftrightarrow 8\ CrO_4^{2-} + 3\ Mn_2O_3\downarrow + 17\ H_2O$ $\quad E = 0.152$

$Cr(OH)_3 + 3\ MnO_4^- + 5\ OH^- \leftrightarrow CrO_4^{2-} + 3\ MnO_4^{2-} + 4H_2O$ $\quad E = \ldots$

Baseline Research Needs

- Baseline fails to oxidize more than 20% of SX-108 (Rapko et al, 2004)
- Recalcitrant species identified in waste (Rapko, 2004; Lumetta & Rapko, 2003)
- Permanganate does not oxidize chromite ($CrFe_2O_4$) or CrOOH (Rapko, 2007)
- Based on bench data; will MnO_2 loading limit glass when scaled up?

TANK	SPECIES
S-111	Chromite $CrFe_2O_4$
S-111	Spinel $CrMn_2O_4$
BY-110	Grimaldite CrOOH
BY-104	Donathite $Fe(Cr,Fe)_2O4$

PROPOSED BASELINE REFINEMENT

Concurrent Use of Multiple Liquid Oxidants

- Permanganate (MnO_4^-)
- Ozonated Water (O_3-H_2O)
- Hydrogen Peroxide (H_2O_2)
- Peroxynitrite ($ONOO^-$)
- Photocatalyst Titanium Dioxide (TiO_2)
- *Peroxyacetate – ($CH_3CO(O)O^-$)*

Possible Benefits

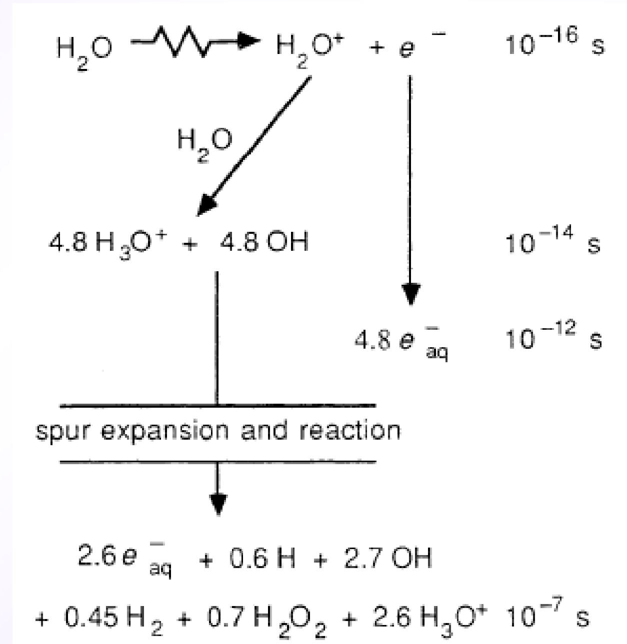
1. *Dissolution of less soluble forms of Cr and possible concurrent application during Al leaching with caustic*
2. *Reduction in Processing Time*
3. *Reduction in mass sent to HLW*
4. *Decrease treatment time*
5. *Destruction of recalcitrant organics*

Proposed Refinement of Baseline: Multiple Oxidants

- Current methods of chromite ore processing are extremely aggressive oxidizing processes:
  - Traditional
    - Kiln Roasting at 1200 C (Zheng et al, 2006)
  - Recent Alternatives
    - 240 ˚C Caustic Leach with 10 Bar O_2 application (Amer & Ibraham, 1996)
    - 300 ˚C Molten Caustic Leach (Zheng et al, 2006)

Free Radical & Other Intermediate Species Formation:

γ-radiation driven reactions
Tank Waste, pH = 13
$H_2O + h\nu \rightarrow O^{\bullet-} + H_2$ or $\rightarrow H_2O^+ + e^-$
$OH^- + h\nu \rightarrow O^{\bullet-} + H^\bullet$ ($OH^\bullet \rightarrow O^{\bullet-} + H^+$ $pK_a = 11.57$)
$NO_3^- + h\nu \rightarrow ONOO^-$
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$
H_2O_2 Added
$H_2O_2 \rightarrow HO_2^- + H^+$ ($pK_a = 11.65$)
$HO_2^- + h\nu \rightarrow O_2^{\bullet-} + H^\bullet$
TiO_2 Added
$>TiO_2 + h\nu \rightarrow TiO_2^+ + e-$
$>TiO_2^+ + 2OH^- \rightarrow O^{\bullet-} + >TiO_2 + H_2O$
O_3 Added
$O_3 + h\nu \rightarrow O_2 + O(^1D)$
MnO_4^- Added
$MnO_4^- + h\nu \rightarrow$? (Swordsma, Tumosa et al. 1971)



Buxton et al. 1988. J. Phys. Chem. Ref. Data 17(2)

Other possible synergistic reactions besides $O_3 + H_2O_2$ producing free radicals? (Holland et al. 2006)

Scoping Experiments

Objectives

- Compare the effectiveness of multiple oxidants to the baseline MnO4- process in chromium oxidation
- Evaluate which combinations of multiple oxidants are most effective in an irradiated environment and non-irradiated environment

Specific Aims

Simulate γ-radiation using 172 nm Ultraviolet (UV) radiation

Systematically evaluate chromium oxidation by combinations of:
MnO_4^-
Ozonated water (O_3-H_2O)
Hydrogen peroxide (H_2O_2)
Peroxynitrite ($ONOO^-$)
TiO_2 photocatalyst

$ONOO^-$ synthesis assumed during 172 nm irradiation of dissolved nitrate (NO_3^-); assumption based on results published in literature

Evaluate effects of chromium concentration and species as well as differing effective oxidant doses

Oxidized Chromium (Cr(VI)) Measured Using the Spectrophotometric Standard Method

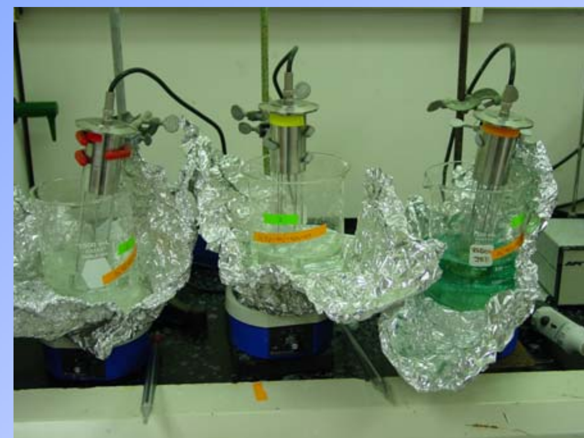
Top: Brian Deskin (MSPH candidate) diluting sample for analysis. Kate Powell (rear) and Vanessa Mastren (Chem Eng) collecting spectrophotometric measurements.

METHODOLOGY

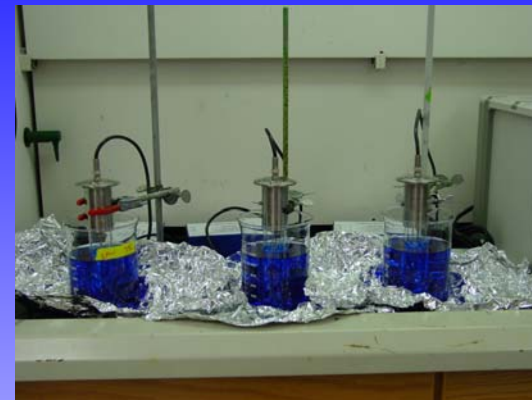
Preliminary Scoping Experiments: Methodology

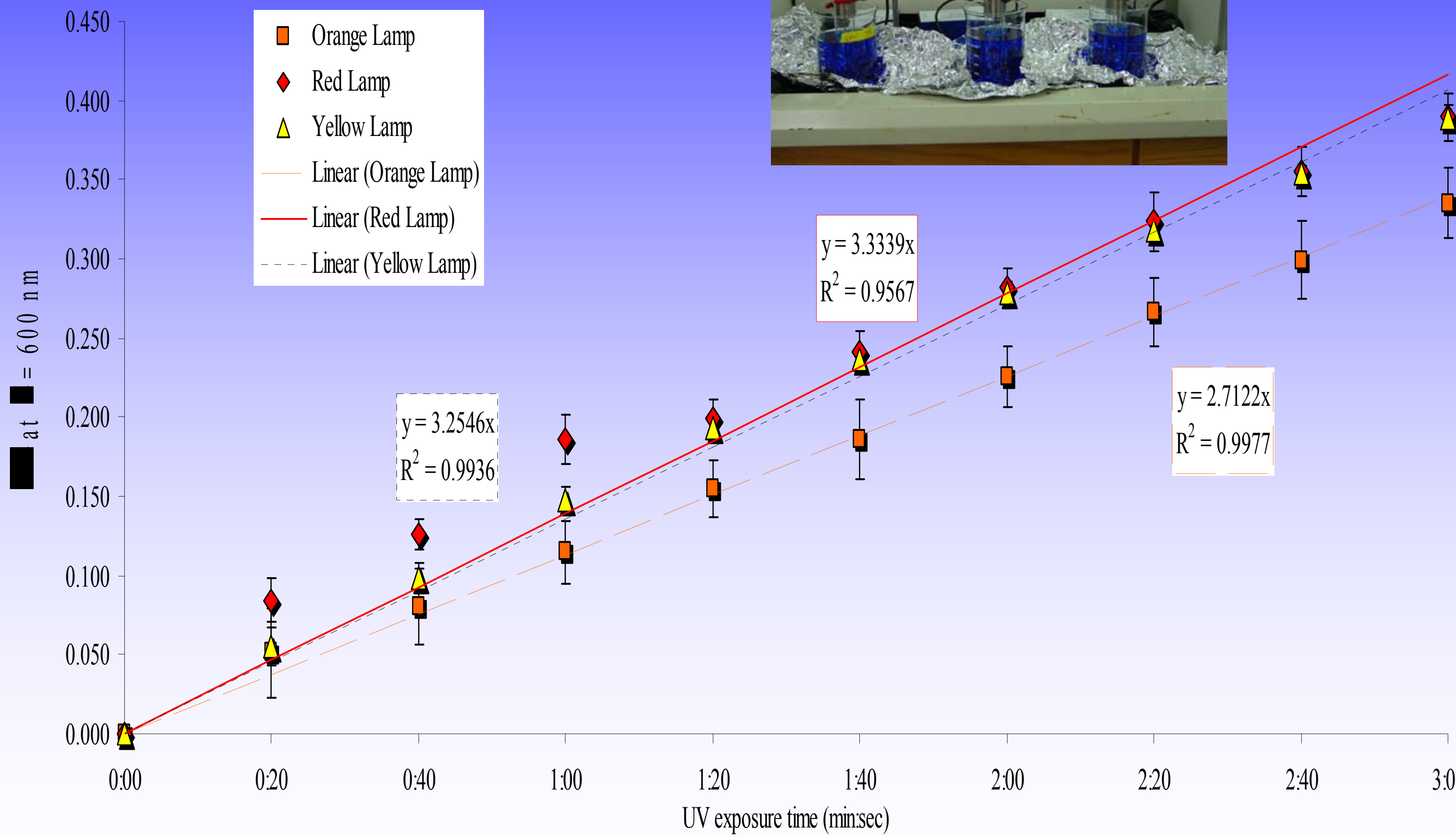
Chromite Waste Simulant OR $Cr(III) = 2.0$ mg/L Solution

- pH adjusted to 13
- Simulate γ-radiation ($\lambda = 0.1$ nm) with 172 nm UV Lamps in some beakers
- $\lambda = 190$ nm threshold for $H_2O \rightarrow OH^{\bullet} + H^{\bullet}$
- Allow reaction with oxidants; Ozonated distilled H_2O (15 – 60 mg/L)
- Measure pH, ORP, T (˚C); Cr(VI) using Standard Spectrophotometric Method

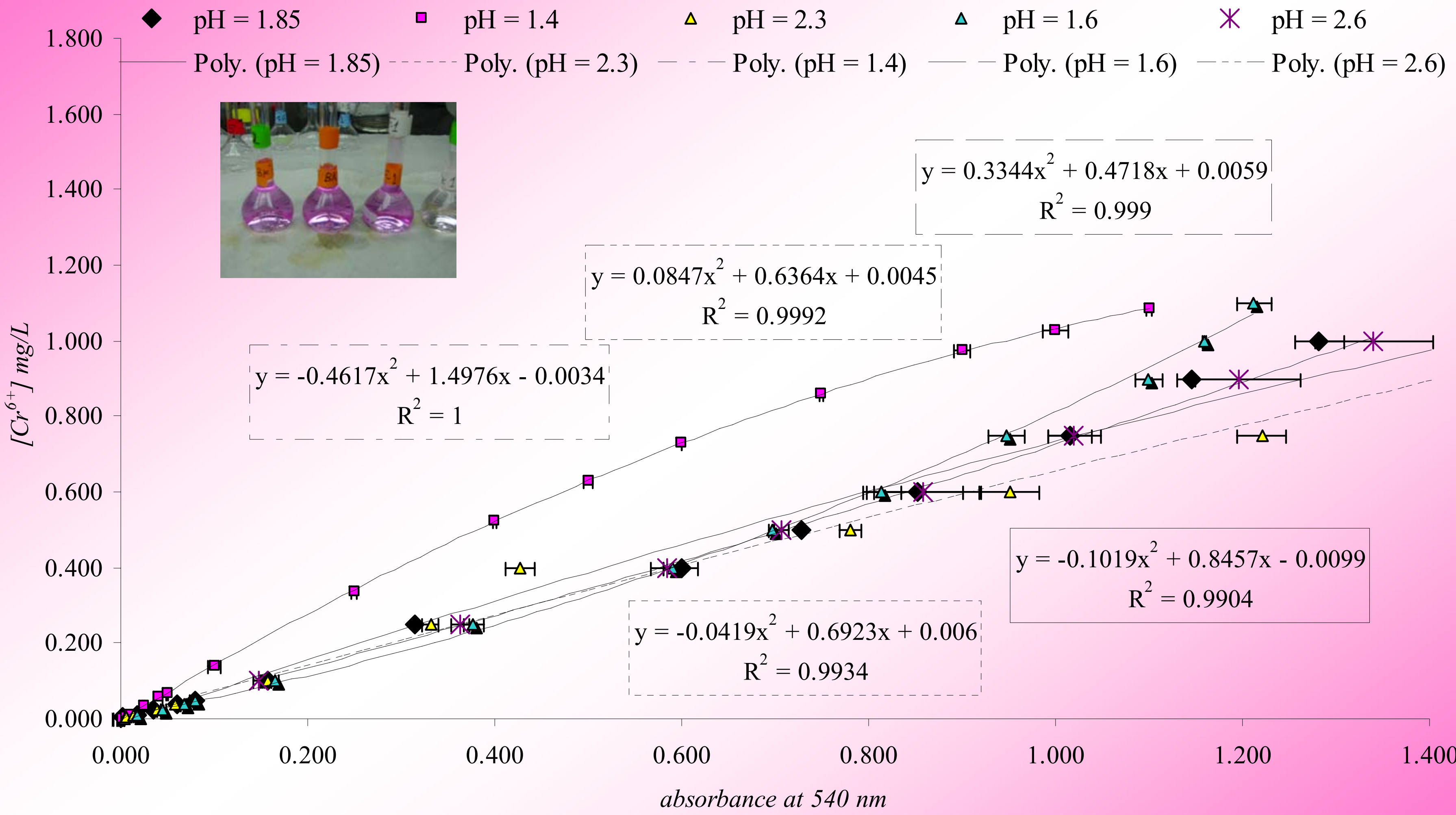


UV Lamps Emission Intensity Check Using Indigo Trisulfonate Solution





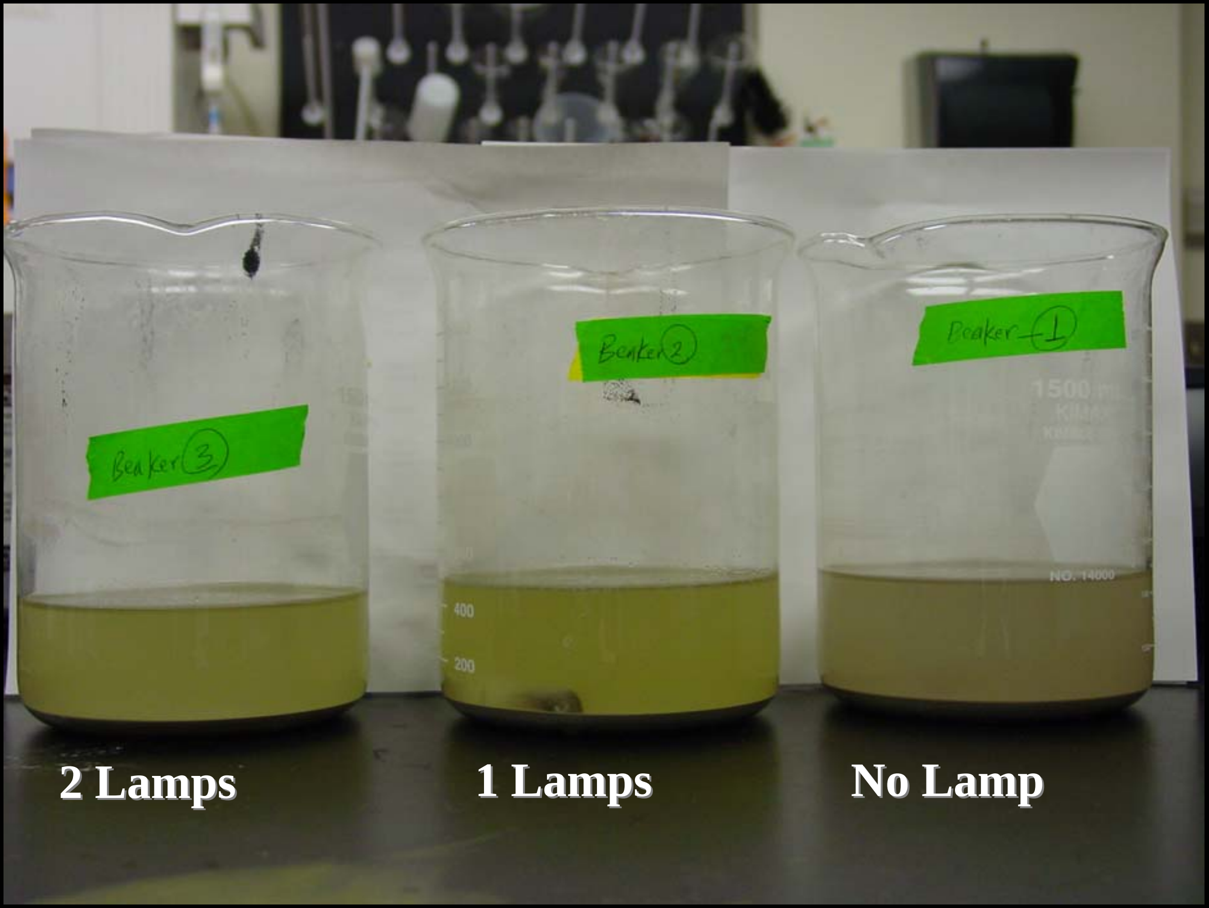
Accuracy in Cr(VI) Detection Using Spectrophotometric Method Through Individual Regressions



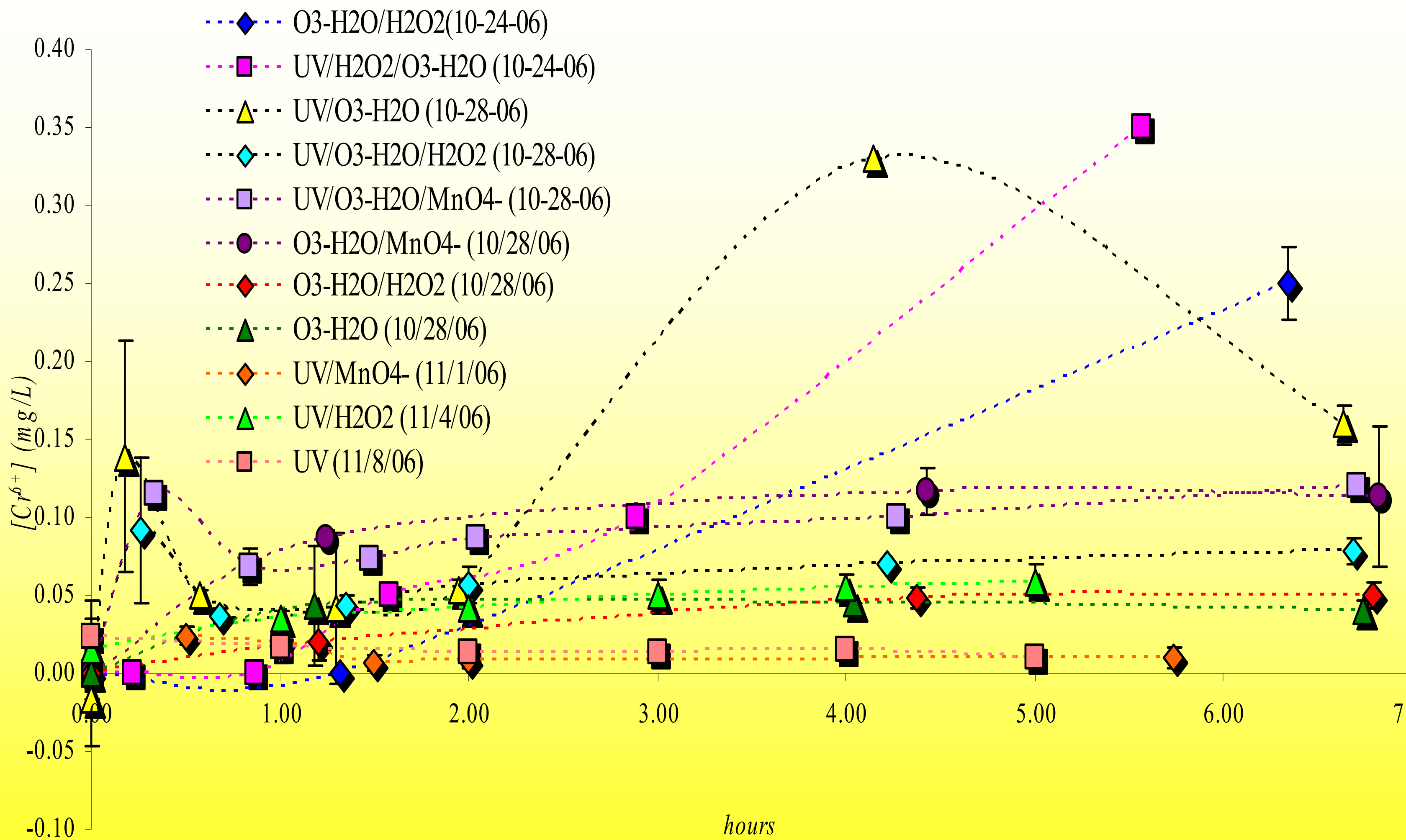
RESULTS

UV Treatment of Waste Simulant

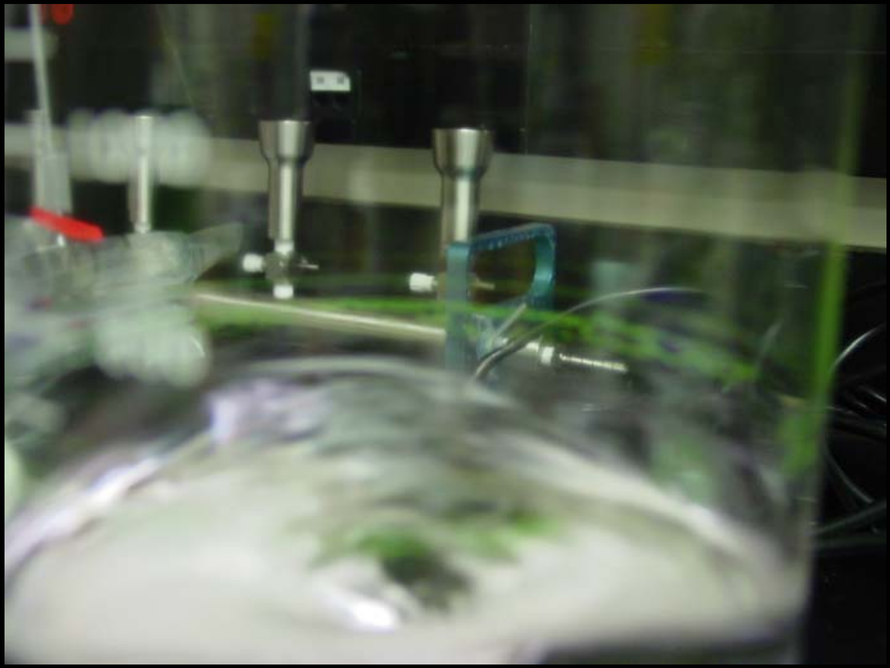
- Production of CrO42- indicated by yellow color of solutions exposed to lamps
- Iron interference prevented spectrophotometric measurement of chromium



Oxidation of Test Solution with Cr_{TOT} = 2.0 mg/L (Cr_2O_3), $[NO_3^-]$ = 30 mg/L



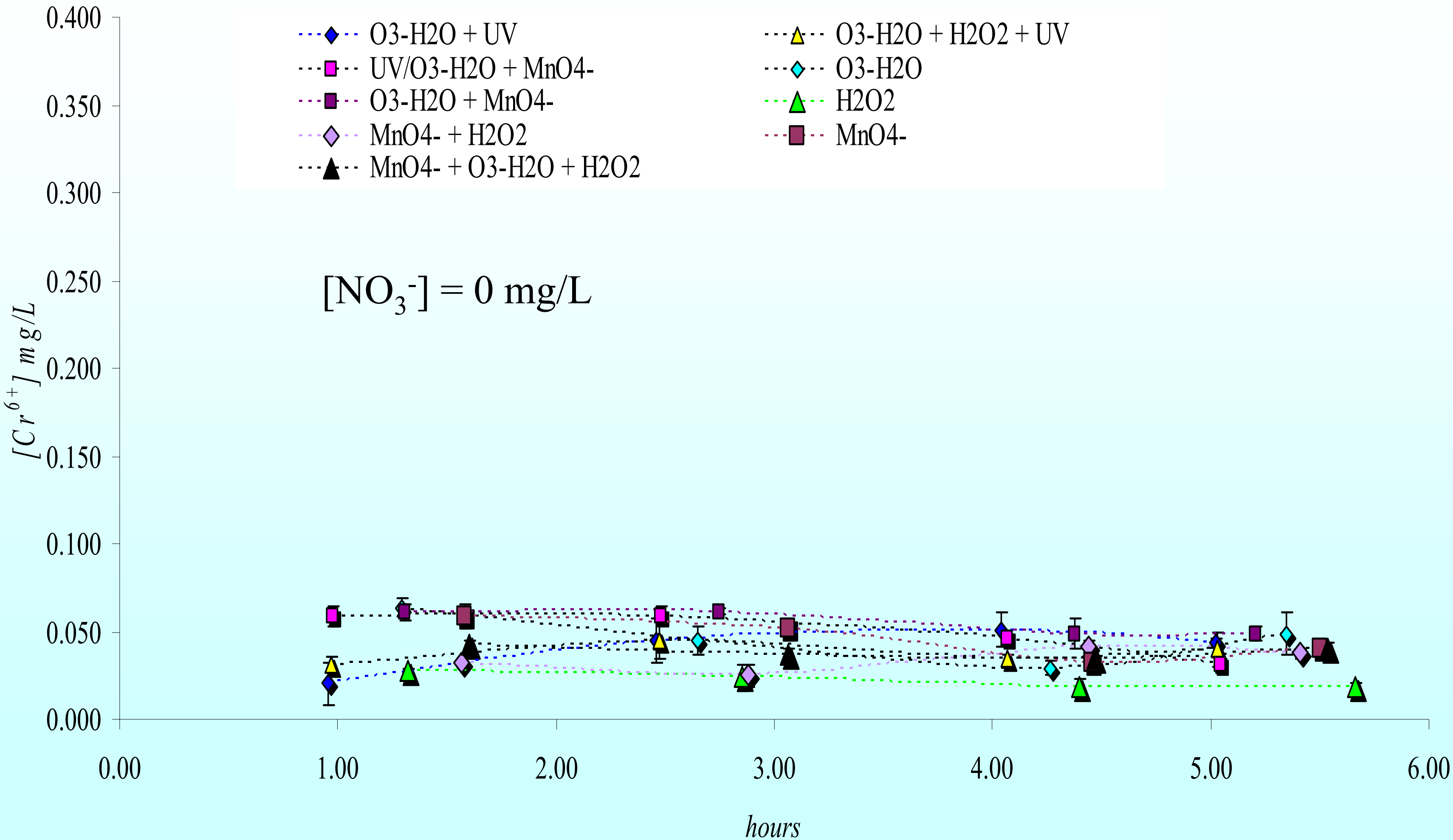
Low Yield of Cr(VI) (Max = 10-20% of $[Cr]_{TOT}$) Due to Cr-Oxide Formation on UV Lamps and Beakers



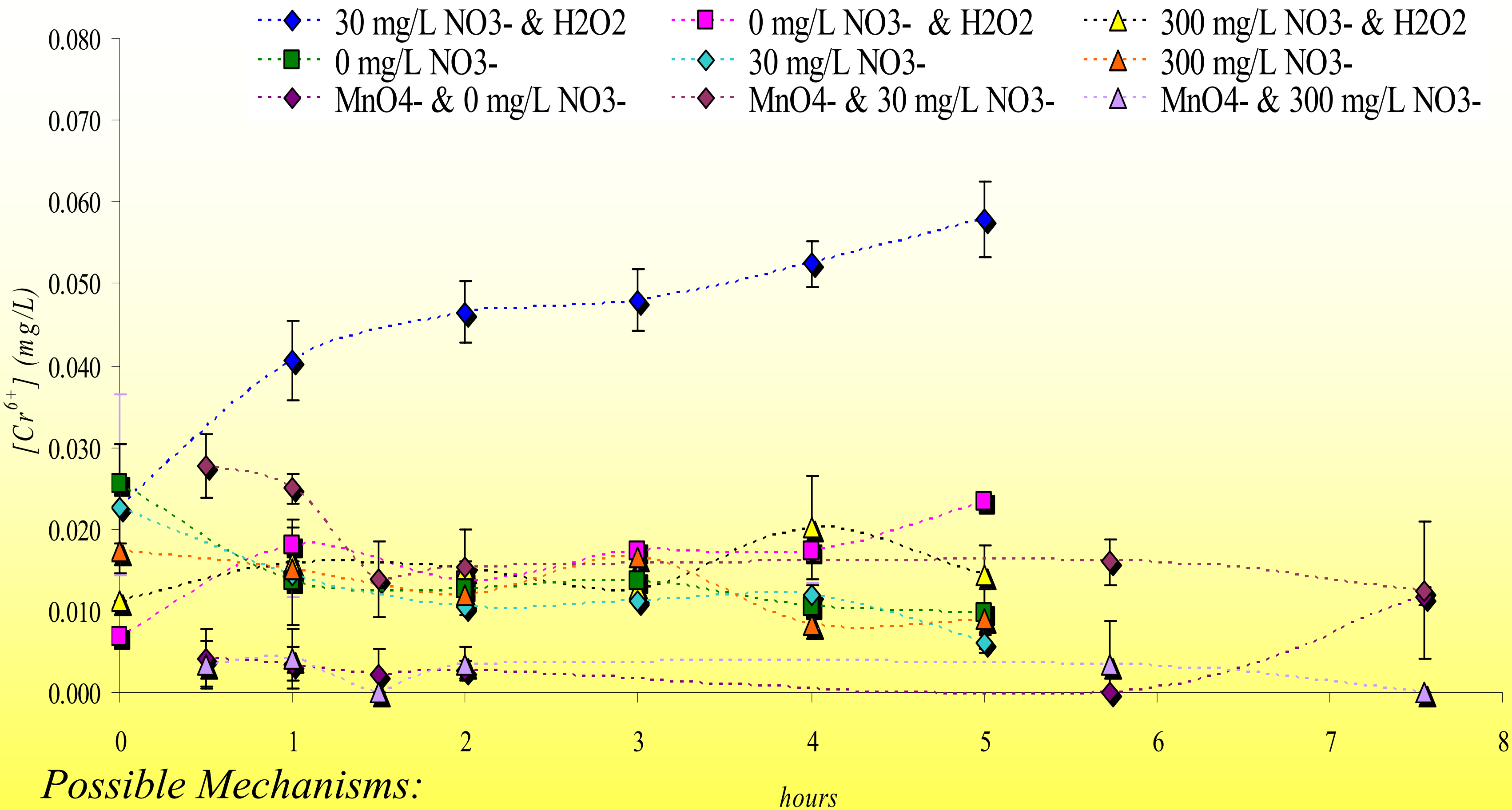
$4Cr^{3+} + 3O_2 + h\nu \rightarrow 2\ Cr_2O_3$

$3O_2 + h\nu \rightarrow O(^1D) + O(3P)$ $O(^1D) + H_2O \rightarrow 2OH^{\bullet}$ $Cr^{3+} + 3OH^{\bullet} + 3e^- \rightarrow Cr(OH)_3$

Irradiated NO_3^- (or $ONOO^-$) Appears to Act Synergistically with O_3-H_2O



Excess [NO_3^-] Suppresses Oxidation/Synergism; Also, Synergism Appears to Occur Strongly with O_3, Mildly with H_2O_2, but not with MnO_4^-



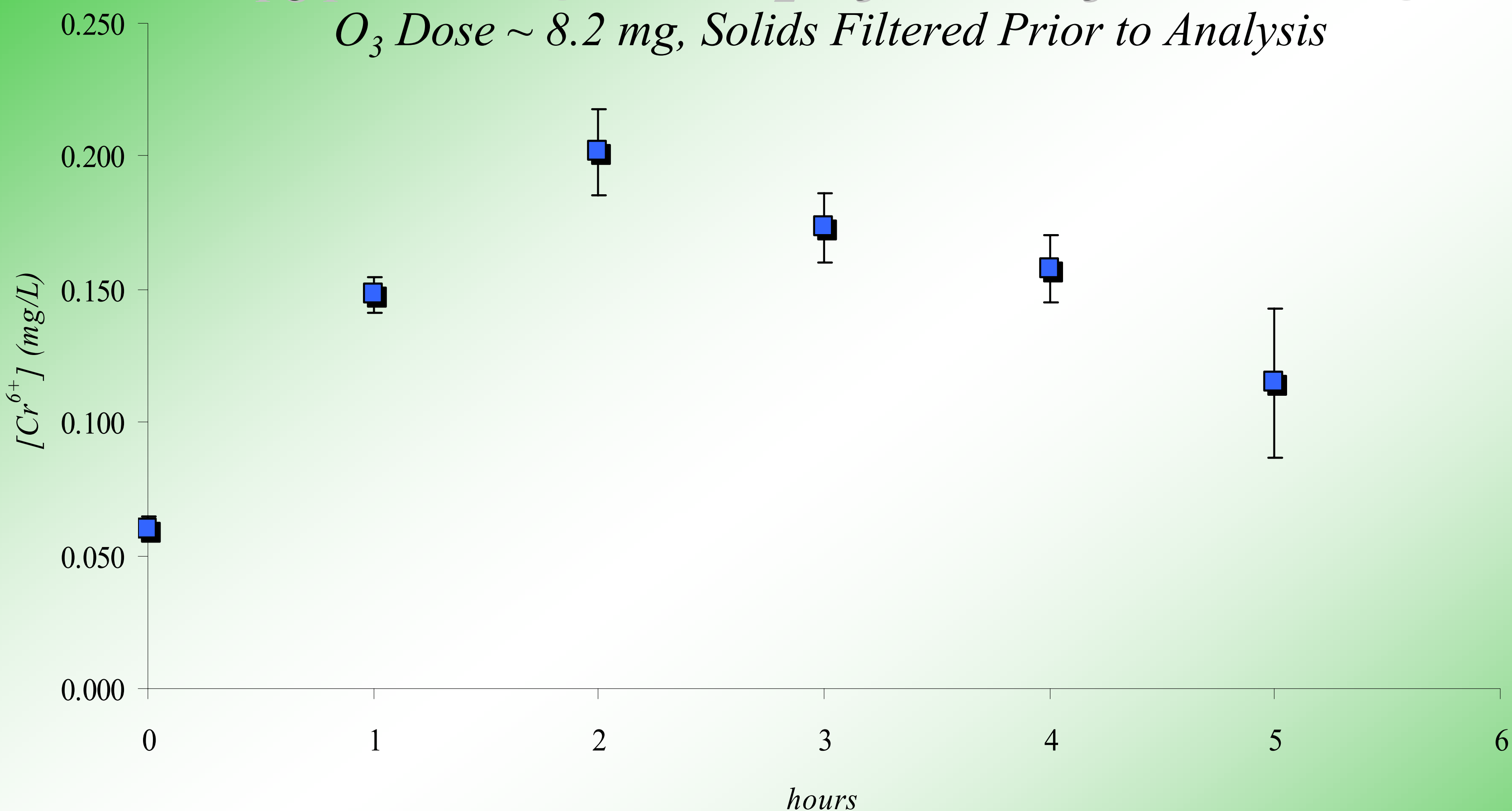
Possible Mechanisms:

$3\ O_3 + ONOO^- + Cr_2O_3 + 4\ OH^- \rightarrow NO_3^- + 2\ CrO_4^{2-} + 3\ O_2 + 2\ H_2O$

$O_3 + ONOO- + 2\ Cr(OH)_3 + 4\ OH^- \rightarrow NO_3^- + 2\ CrO_4^{2-} + H_2O + 4\ H_2O_2$

$2\ O_3 + 2\ ONOO^- + 2\ Cr(OH)_3 + 4\ OH^- \rightarrow 2\ NO_2^- + 2\ CrO_4^{2-} + 5\ H_2O_2$

UV + O_3-H_2O Effectiveness in Test Solution of Cr_{TOT} = 5.0 g/L (Cr_2O_3), [NO_3^-] = 30 mg/L

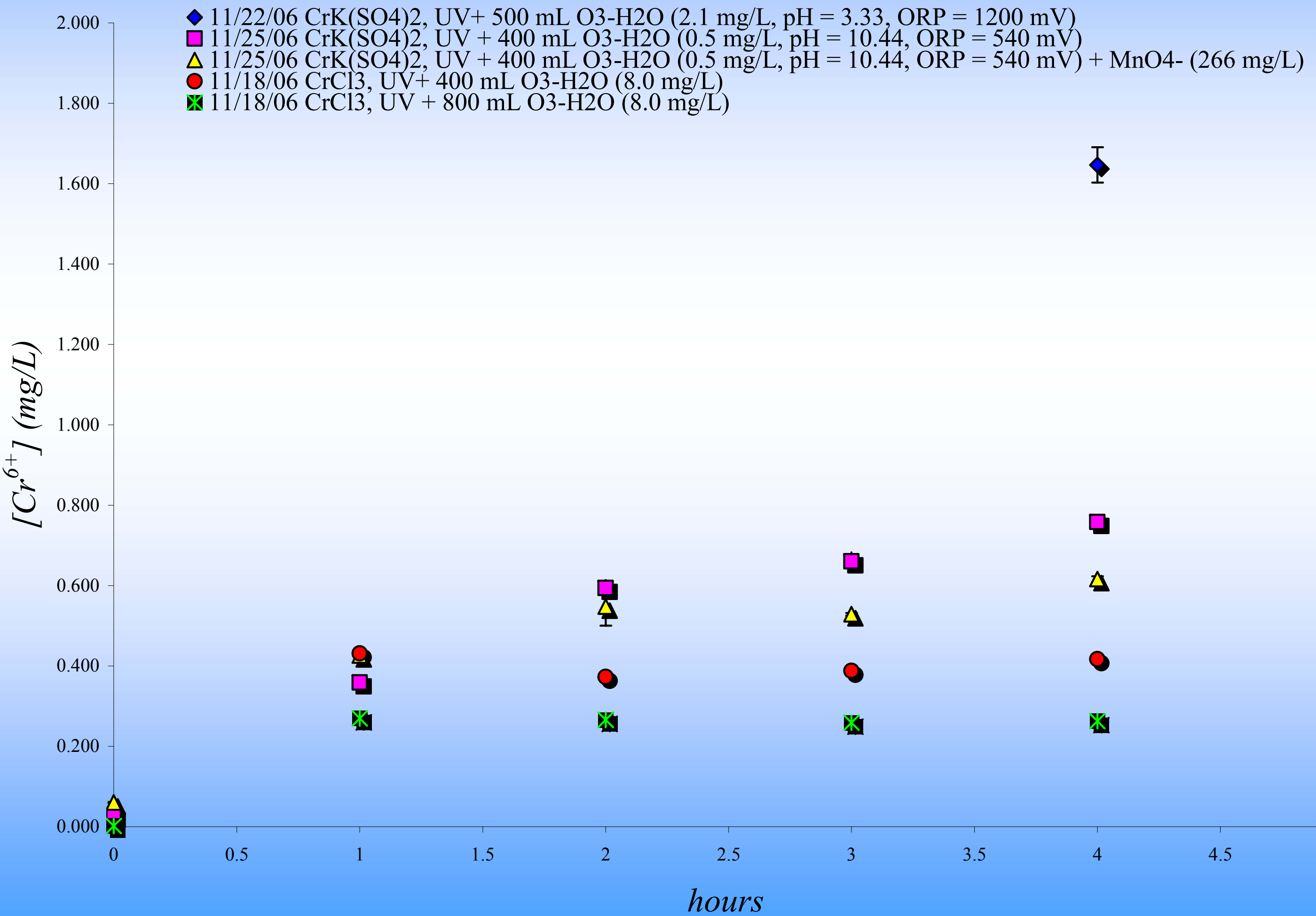


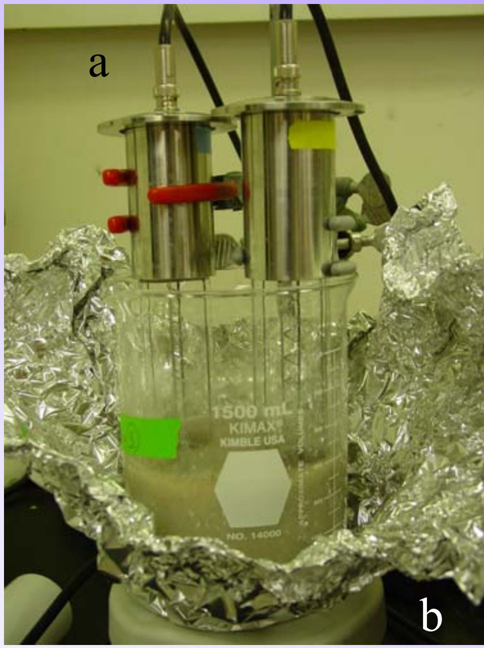
Trend of CrO_4^{2-} to decline with treatment time:

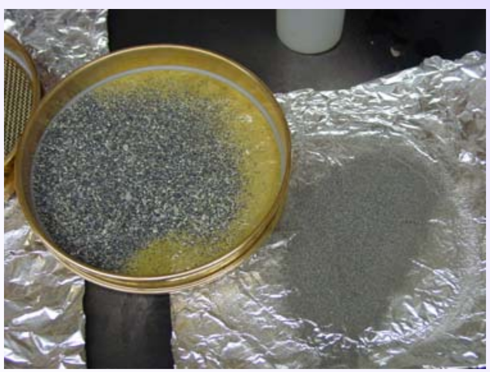
Possible CrO_4^{2-} sorption to Cr_2O_3 solids OR CrO_4^{2-} reduction to $Cr(OH)_3$

UV + O_3-H_2O + $ONOO^-$ Effectiveness for Different Cr(III) Salts and at Differing O_3 Doses

Cr_{TOT} = 2.0 mg/L and $[NO_3^-]$ = 30 mg/L in all cases







Path Forward

- Further Downselect Combinations at Bench Scale on Waste Simulant with Simulated Gamma Irradiation (172 nm Ultraviolet)
  - Initial screening of all previously tested combination plus peroxyacetate (CH_3COOO^-) which may concurrently facilitate aluminum dissolution
  - Retain most effective combinations to evaluate effects of
    - Oxidant dose (esp., increase mass loading of ozone in water)
    - Irradiation Dose
    - Simulant component concentrations (i.e. NO_3^-, oxalate, nitrite)
    - Simulant particle size
    - Chromium species (i.e. chromate (Cr_2FeO_4) or CrOOH)
    - Temperature
  - Use ICP-MS to measure total chromium in filtered liquid fraction,
    - Measures (Cr(III) + Cr(VI)) in supernate
    - Removes interference of MnO_4^-
    - Removes interference of aluminum (Cr(VI) can sorb to colloidal aluminum)

a) Preliminary test of a double UV dose in a Chromite Waste Simulant b) Sieving Ground Chromite

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