

Chromate treatment for soils and water

Hudson County Chromate production waste sites

K.L.K Environmental Group LLC

and

Uni Chem Inc

2005-2007

- 160 sites contaminated with Cr(VI) from Chromite ore processing residues (Chromate waste)
- Polluters were PPG Industries, Allied Signal/ (Honeywell) and predecessors of Occidental Chemical Corp, Maxus Energy Corp and Chemical Land Holdings
- Presently most sites are asphalt capped and monitored periodically
- Some sites have been remediated

Now we have a simple technology for fast remediation of Chrome (VI) contaminated sites

New developments

- Chrome moratorium lifted on Feb 14th 2007 (past date)
- Residential areas may not contain above 20ppm of Cr(VI)- old standard was 240ppm
- Commercial standards have not been finalized
- Hexavalent Chromium (Cr (VI)) is hazardous to humans. Long term exposures is associated with lung cancer –remember Erin Brokovich
- It affects 184 sites in Hudson County

New technology reduces Cr (VI) concentrations in soils to levels below 2 ppm

Our new technology consists of:

1. Quantitative reduction of the Chromate(Cr(VI)) existing in the soil and water using a non-toxic reducing agent. The reduced form is Cr(III) . Trivalent Chromium is non-toxic.
2. Immobilization of resulting trivalent Chromium in the soil to prevent re-oxidation and migration of this species

Chemistry

I. (reduction)



pH = [4.5, 5.5]

Quantitative reduction- Chromium III less than <1ppt

II. (immobilization)



-extremely insoluble

The Dichromate/Sulfite Cell

- To calculate the final concentration of Cr(VI) in the soil

$$E = E_{red} + E_{ox}$$

$$E = 1.33 - \left\{ (0.0592/6) \log \left(\frac{[\text{Cr}_{(3+)}]^2}{[\text{Cr}_2\text{O}_7^{(2-)}] [\text{H}_{(+)}]^{14}} \right) \right\}$$

$$E = -0.17 - \left\{ (0.0592/2) \log \left(\frac{[\text{SO}_4^{(2-)}] [\text{H}_{(+)}]^2}{[\text{SO}_2]} \right) \right\}$$

$$E = 1.16 - \left\{ (0.0592/6) \log \left(\frac{[\text{Cr}_{(3+)}]^2 [\text{SO}_4^{(2-)}]^3}{[\text{Cr}_2\text{O}_7^{(2-)}] [\text{SO}_2]^3 [\text{H}_{(+)}]^8} \right) \right\}$$

$$E = 1.16 - \left\{ [(0.0592/6) \times 8\text{pH}] \right\} - \left\{ (0.0592/6) \log \left(\frac{[\text{Cr}_{(3+)}]^2 [\text{SO}_4^{(2-)}]^3}{[\text{Cr}_2\text{O}_7^{(2-)}] [\text{SO}_2]^3} \right) \right\}$$

$$E = 1.16 + \left\{ [0.07895\text{pH}] \right\} - \left\{ (0.0592/6) \log \left(\frac{[\text{Cr}_{(3+)}]^2 [\text{SO}_4^{(2-)}]^3}{[\text{Cr}_2\text{O}_7^{(2-)}] [\text{SO}_2]^3} \right) \right\}$$

- But:

In the phosphate system $[\text{Cr}_{(3+)}] \leq 1.91 \times 10^{-7} \text{ M}$

$$E = 1.16 + 0.07895\text{pH} - \left\{ (0.0592/6) \log (1.91 \times 10^{-7})^2 - \right. \\ \left. \left((0.0592/6) \log [\text{SO}_4^{(2-)}]^3 / [\text{Cr}_2\text{O}_7^{(2-)}][\text{SO}_2]^3 \right) \right\}$$

$$E = 1.16 + 0.07895\text{pH} + 0.13261 - \left\{ (0.0592/6) \log ([\text{SO}_4^{(2-)}]^3 / \right. \\ \left. [\text{SO}_2]^3) \right\} + \left\{ (0.0592/6) \log ([\text{Cr}_2\text{O}_7^{(2-)}]) \right\}$$

$$E = 1.29261 + 0.07895\text{pH} - \left\{ (0.0592/2) \log ([\text{SO}_4^{(2-)}] / \right. \\ \left. [\text{SO}_2]) \right\} + 0.0592 \log [\text{Cr}_2\text{O}_7^{(2-)}]$$

SO_2 is applied in a 50% excess

- The maximum ratio of $[\text{SO}_4^{(2-)}] / [\text{SO}_2] = 2$

- The term $-\left\{ (0.0592/2) \log ([\text{SO}_4^{(2-)}] / [\text{SO}_2]) \right\} = 8.9120 \times 10^{-3}$

Now we have:

i. $283698 + 0.07895\text{pH} = -0.0592 \log[\text{Cr}_2\text{O}_7]$ or

ii. $6804265 + 1.33338963\text{pH} = -\log[\text{Cr}_2\text{O}_7]$

<u>pH</u>	<u>21.6804265 + 1.33338963pH</u>	<u>[Cr₂O₇(2-)]</u>
0	21.6804	2.6874×10^{-22}
1	23.0138	9.6872×10^{-24}
2	24.3472	4.4957×10^{-25}
3	25.6806	2.0864×10^{-26}
4	27.0140	9.6828×10^{-28}
5	28.3474	4.4937×10^{-29}
6	29.6808	2.0855×10^{-30}
7	31.0142	9.6783×10^{-32}
8	32.3476	4.4916×10^{-33}

1 mole of [Cr₂O₇ (2-)] contains ~ 104 g of Cr

■ Therefore:

For the pH range of 4-7 the residual ppms of Cr (VI) are:

pH	Cr
4	1.007x10 ⁻¹⁹ ppm to 1.007x10 ⁻¹³ ppt
5	4.6734x10 ⁻²¹ ppm to 4.6734x10 ⁻¹⁵ ppt
6	2.16892x10 ⁻²² ppm to 2.16892x10 ⁻¹⁶ ppt
7	1.0065x10 ⁻²³ ppm to 1.0065x10 ⁻¹⁷ ppt

Experimental (pilot test)

20 gallon fish tanks were filled up with soil samples and 4 injection ports were set in each tank at the same intervals. The reducing solution containing a phosphate buffer , pH \sim 4.5- 5.0 and sodium sulfite was pumped into the ports

- The solution used for the reduction of the Hexavalent Chromium was made in this way:
 1. 7.6 kg of Di-sodium Phosphate anhydrous
 2. 5 liters of Phosphoric Acid 85%
 3. 6.0 kg of Na_2SO_3
 4. 15 gallons of de ionized water
- Total volume: 20.6 gallons
- The reaction temperature is 18-20° C

A total of 6.974 gallons of solution were pumped into the fish tanks

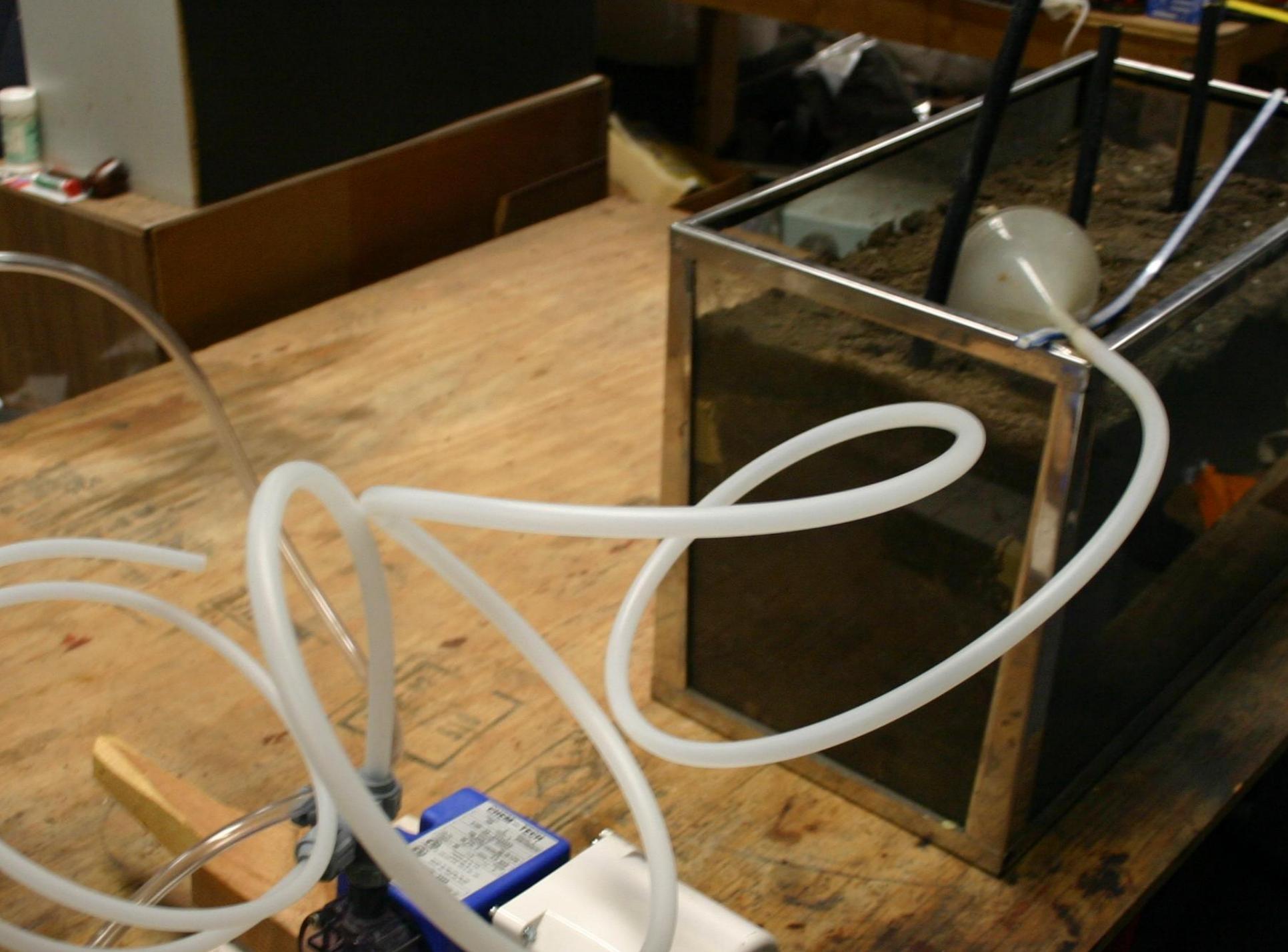
Experimental setting

- *A 20 gallon fish tank filled up with soil.*

Tank 1	Cr(VI) (ppm)	Total Chromium (ppm)	Cr(III) (difference)
Initial	5050	7360	2310
After treatment	<<10	7390	7390

Tank 2	Cr(VI) (ppm)	Total Chromium (ppm)	Cr(III) (difference)
Initial	4390	6600	2210
After treatment	<<10	Not analyzed	-

Tank 3	Cr(VI) (ppm)	Total Chromium (ppm)	Cr (III) (difference)
Initial	6326	9220	2894
After treatment	<<10ppm	9220	9220



Leach ate

Samples of treated soil were set into a chromatographic column with a fine fritted glass filter on the bottom. The soil was soaked in a 0.5M buffer ,Sodium Acetate/ Acetic Acid pH5 for 3 days before filtration.No Chromium (III) was found in the filtrate.

Kinetics: Between pH 4.5 to 5.5 it takes less than 5 minutes for completion of the reaction

Experience prove

1. Chromium (VI) is reduced to Chromium(III)
2. Chromium(III) is fixed in the soil matrix
3. The reaction is fast and efficient both for the reduction as for the fixation of Chromium(III) as phosphate
4. The reaction is pH dependent

How fast it goes under what conditions

Kinetics of the reduction of Chromates with Sulfite- pH and effect

At a pH range of 4 to 6 the major species is CrO_4^{2-} we will be measuring the concentration change expressed as:

$$d [\text{CrO}_4^{2-}] / dt$$

This expression is a function of the pH, concentration of CrO_4^{2-} , concentration of HSO_3^- and the temperature using a buffer we fix the pH. The concentration HSO_3^- is 0.2M a value that will not change much is the reaction, because the maximum concentration of Chromate used is in the 10^{-3}M order .

We are going to calculate the concentration using the Lambert and Beer's Law :

$$A = \epsilon l c$$

■ *For Chromate*

$$\epsilon = 4820 \text{ L x mol}^{-1} \text{ x cm}^{-1}$$

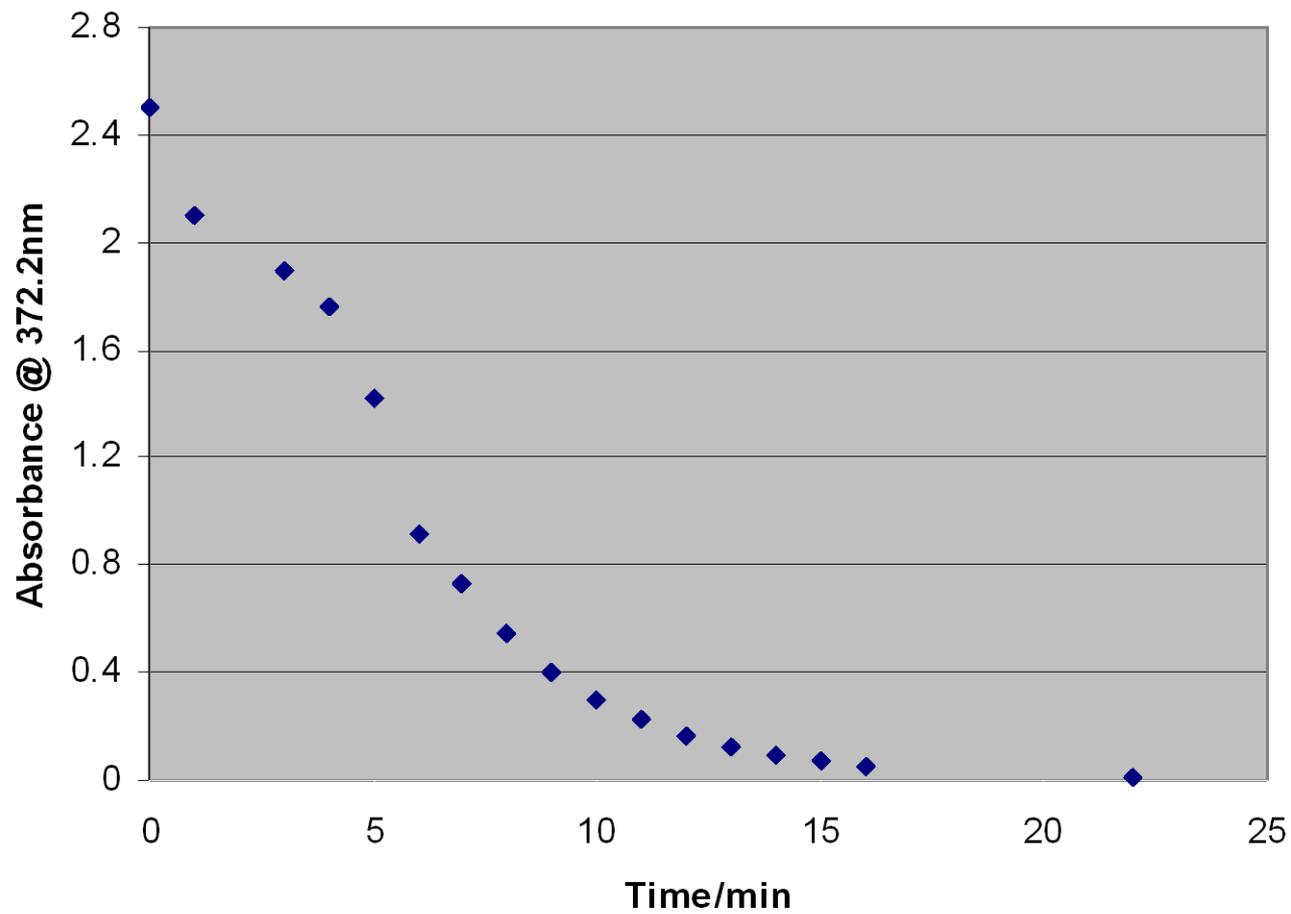
$$\lambda = 1 \text{ cm (cell path)}$$

$$C(\text{Molar}) = A / \epsilon \lambda = A / 4820 \text{ mol/L}$$

$$C(\text{ppm}) = C(\text{molar}) \times \text{atomic mass of Cr} \times 10^6 / 10^3$$

$$C(\text{ppm}) = 52 \times C(\text{molar}) \times 10^3$$

Fig. 1.1 Kinetics of The Reduction of Dichromate with Sulfites at pH 6



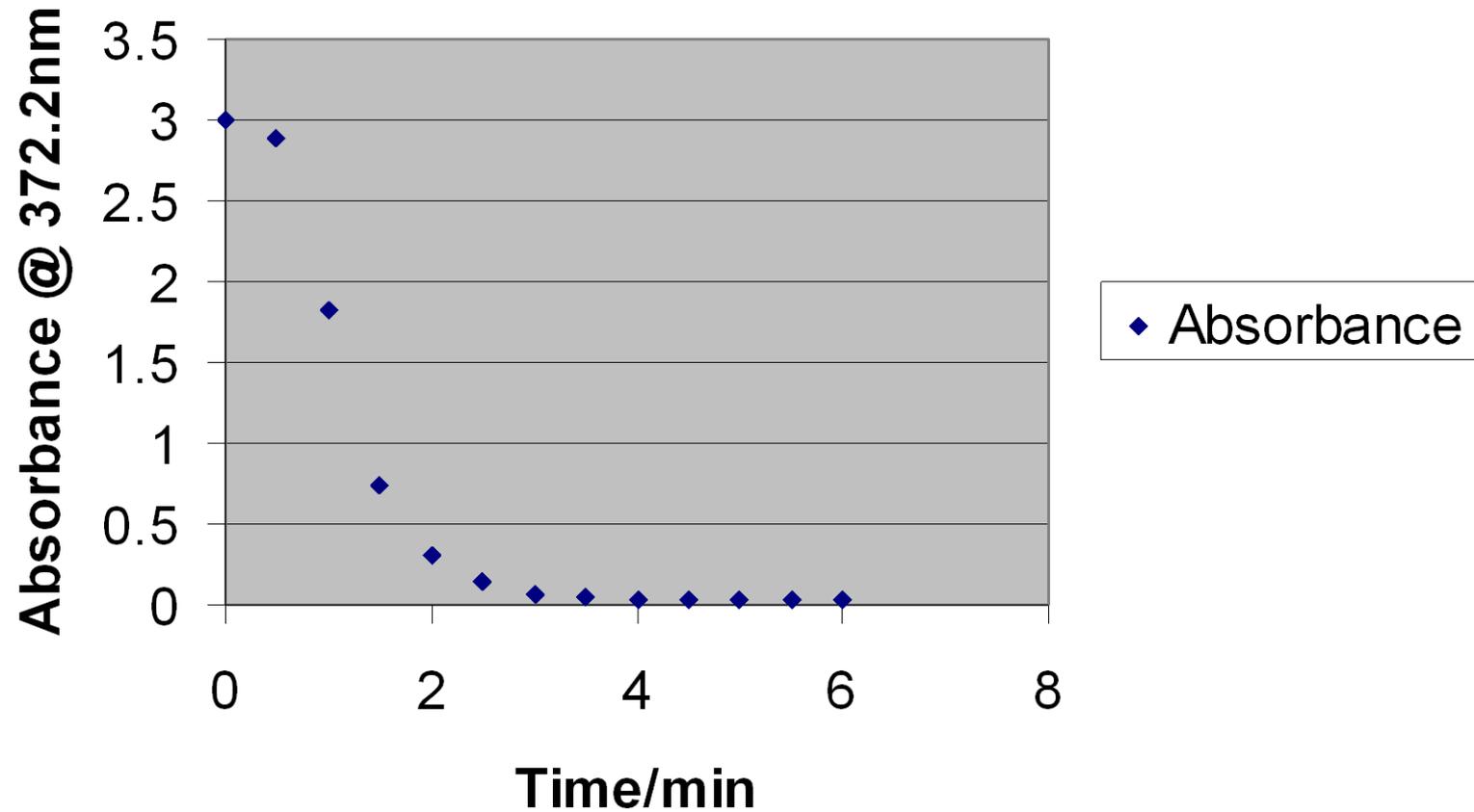
■ For Fig 1.1

pH=6

T(min)	A	C(mol)	C(ppm)
0	2.5	5.21×10^{-4}	27.10
17	0.012	2.5×10^{-6}	0.13

The concentration goes from 27.10 ppm to 0.13 ppm in 17 minutes.

Fig. 2.1 kinetics of the Reduction of Dichromate by sulfites @ pH 4.5



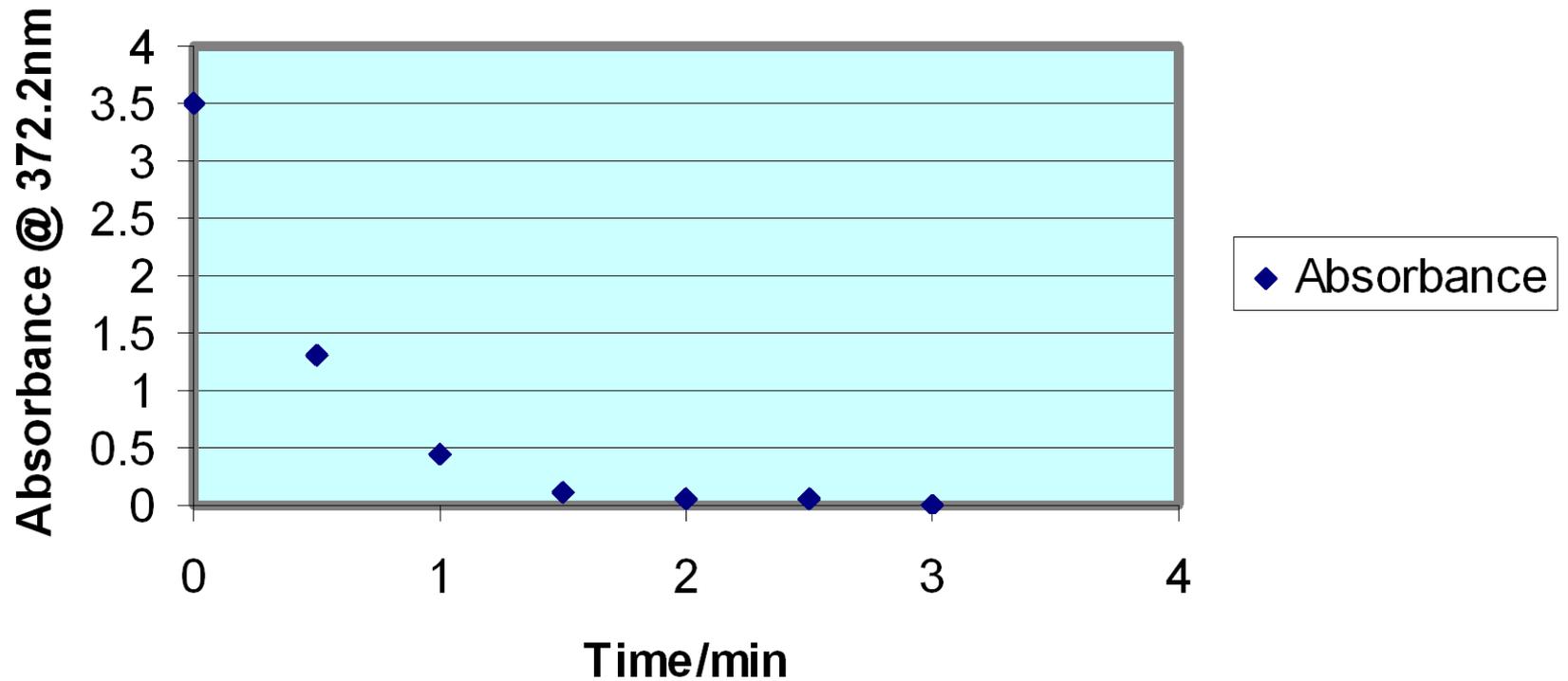
■ For Fig 2.1

pH=4.5

T(min)	A	C(molar)	C(ppm)
0	3.0	6.22×10^{-4}	32.37
4	0.035	7.26×10^{-6}	0.38

In 4 minutes the concentration dropped from 32.37 ppm to 0.38 ppm

Fig 3.1 Kinetics of the Reduction of Dichromate By Sulfites
@ pH 5



- For Fig 3.1 pH=5

T(min)	A	C(molar)	C(ppm)
0	3.50	7.26×10^{-4}	37.75
1.5	0.105	2.18×10^{-6}	1.13
2.5	0.056	1.17×10^{-5}	0.61

In 15 minutes the concentration dropped to 1.13- after it goes slowly.

The ideal pH range from these results is 4.5 to 5.0

Fig. 1.2 Kinetics of the Reduction of Dichromate by Sulfites @ pH 6

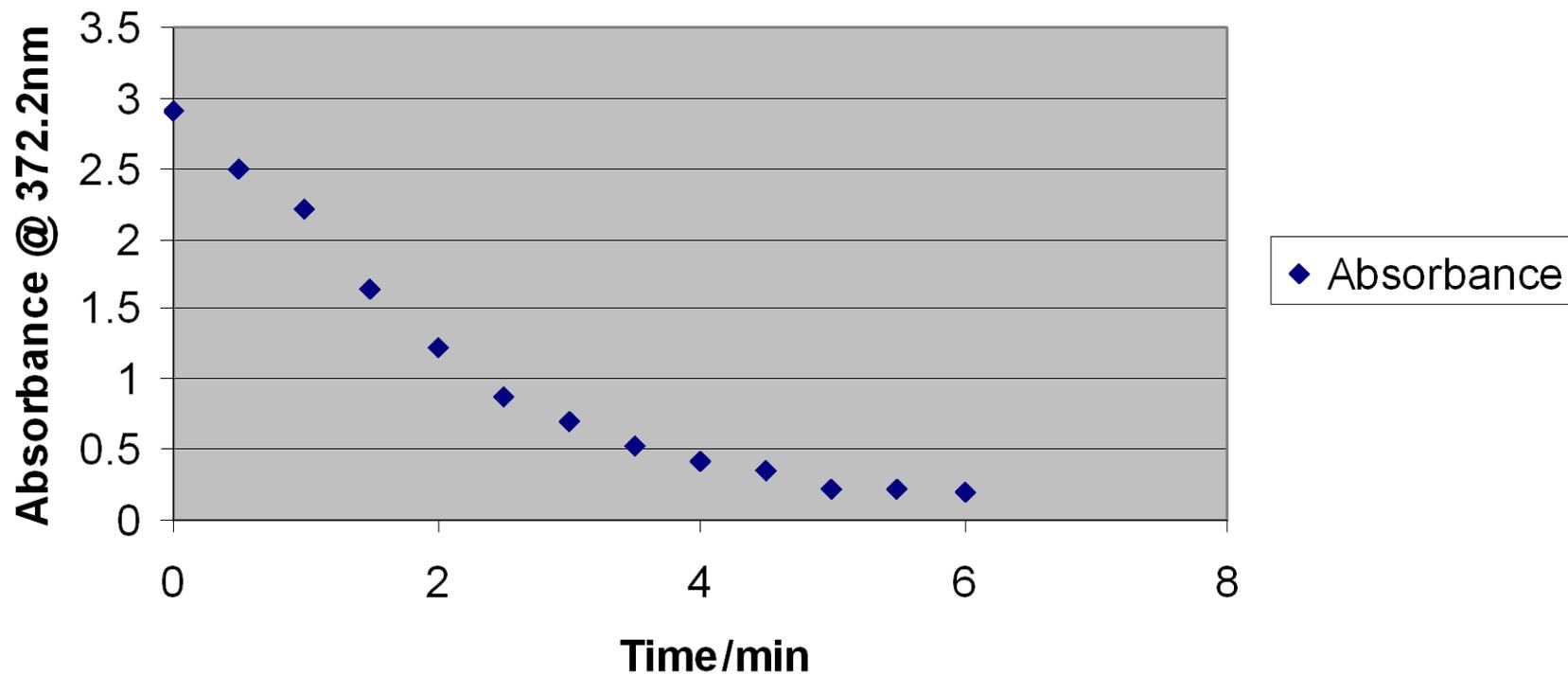


Fig 1.2

pH=6

T(min)	A	C(molar)	C(ppm)
0	2.90	6.02×10^{-4}	31.29
0.5	2.50	5.19×10^{-4}	26.97
1.0	2.20	4.58×10^{-4}	23.83
1.5	1.64	3.40×10^{-4}	17.69
2.0	1.23	2.55×10^{-4}	13.27
2.5	0.88	1.85×10^{-4}	9.49
3.0	0.70	1.45×10^{-4}	7.55
3.5	0.53	1.10×10^{-4}	5.72
4.0	0.421	8.73×10^{-5}	4.54
4.5	0.35	7.26×10^{-5}	3.78
5.0	0.21	4.35×10^{-5}	2.27
5.5	0.22	4.56×10^{-5}	2.37
6.0	0.19	3.94×10^{-5}	2.05

Is it possible to reoxidize the Cr(III) to Cr(VI)

A few experiments were done:

- Preparation of a solution of Cr⁺³ (III) at pH= 3, 5, 7, 9, 11

A 0.01M solution of Cr (III) chloride different pH was set in a glass bottle (500ml) 300ml of solution. An airstone connected to an air pump was set inside. Air was bubbled continuously for 10 days at room temperature.

Result: no reoxidation

- Oxidation of Cr(III) using hydrogen peroxide
30%

Several suspensions of CrPO_4 in phosphate based buffers were reacted with 30% H_2O_2 under constant stirring. The pH was regulated from 4 to 11 with one unit of pH of increment from experiment to experiment at RT.

Results: no oxidation

But at $\text{pH} > 13$ some reoxidation occurs in solution of Cr(III) with hydrogen peroxide

- Oxidation with 12.5 % Cl₂ solution (bleach)

Most of the Cr (III) is reoxidized to Cr (VI) chromate in 10 minutes.

Use of reagents

From experimental tests we know that we need 5.0 lb of sodium bisulfite per pound of Cr (VI) to be reduced per cubic yard

**Effective application of the
sulfite/buffer solution in soils to
reduce all Cr (VI) to Cr (III) (CrPO_4)**

To minimize the diffusion of Cr (VI) and to maximize its reduction to Cr (III) there are two alternatives:

1. Mixing the soil with the solution using soil mixing technology (see Allu Technology – Finland)
2. Using perforated pipes able to diffuse uniformly the solution in the soil

Conclusions

We have a method of reduction of chromates to Cr (III) with the following features:

1. Chromates are reduced quantitatively (less than 2ppm left) to Cr (III) in few minutes (2-4 min).
2. Cr (III) formed is in the form of the extremely insoluble phosphate. Therefore Cr (III) will not leach out of the soil .
3. This procedure can be applied to Cr (VI) contaminated ground waters.
4. Under normal conditions no reoxidation of Cr (III) to Cr (VI) occurs.
5. The application process for soil remediation are simple and relatively inexpensive. Only 5lb of sodium bisulfite are required to reduce 1lb of Cr (VI) per cubic yard of soil

Besides

- The chemicals used in the remediation are cheap and of low toxicity
- A finnish company Allu, represented in NJ as the Allu Group provides the adequate technology for a fast remediation of Cr (VI) contaminated areas