APPENDIX

List of figures

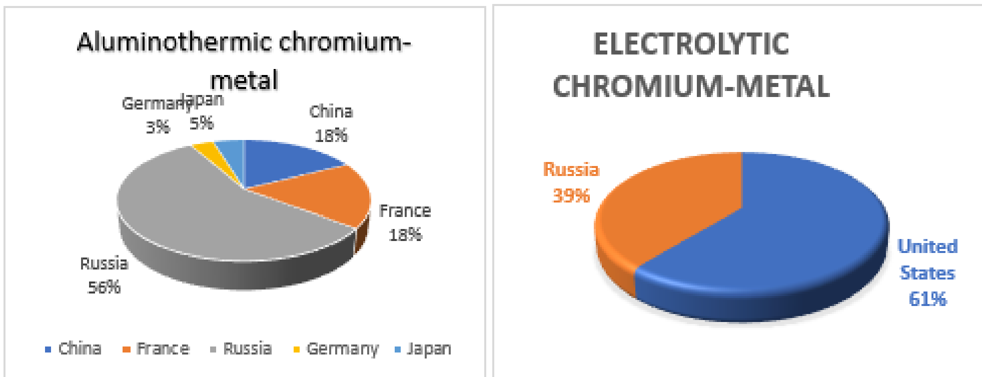
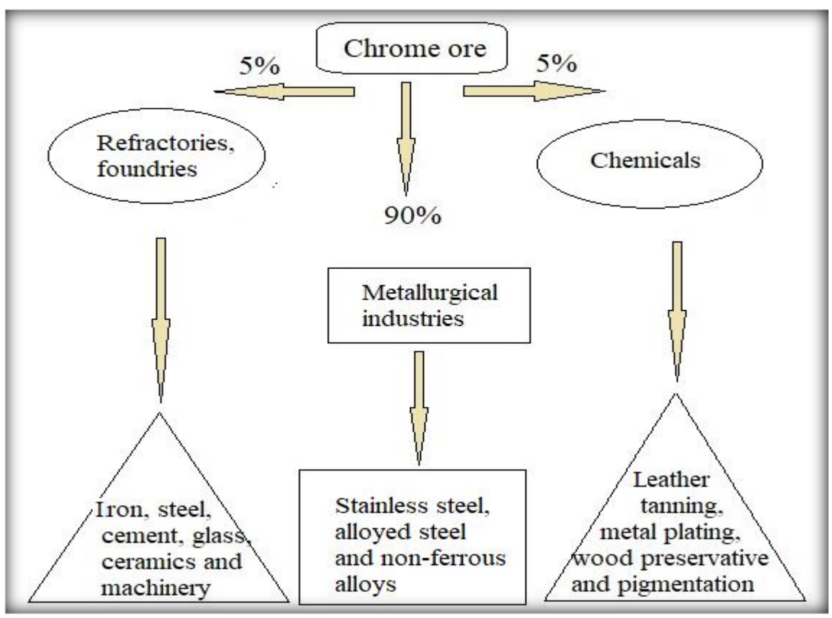


Figure 1:Global major producers - manufacturers of aluminothermic and electrolytic chromium-metal. (National Research Council 1995).



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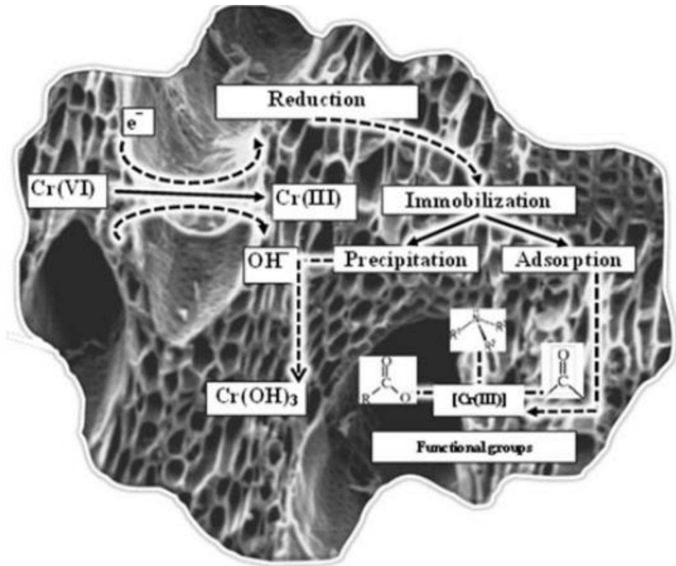

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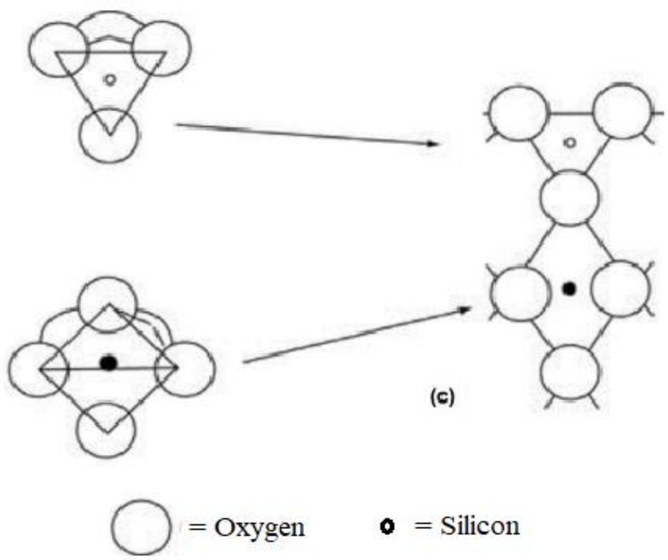


Figure 4. Tetrahedrally co-ordinated (a), octahedrally co-ordinated (b); cation polyhedrons (c) linked octahedral and tetrahedral polyhedrons (Huggett, 2004).

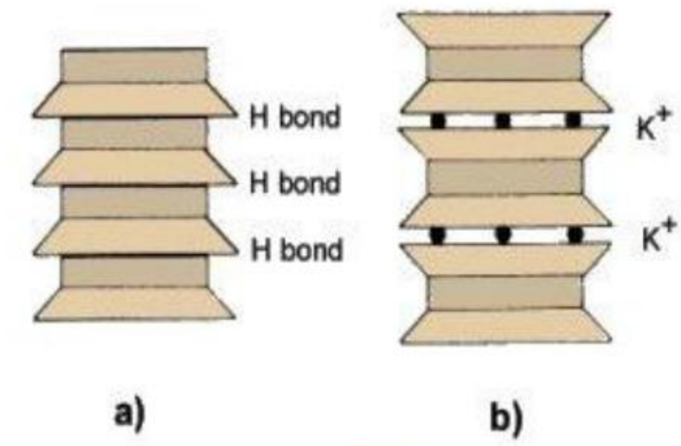


Figure 5. Structure of a) kaolinite b) Illite. (Ayadi et al., 2013)

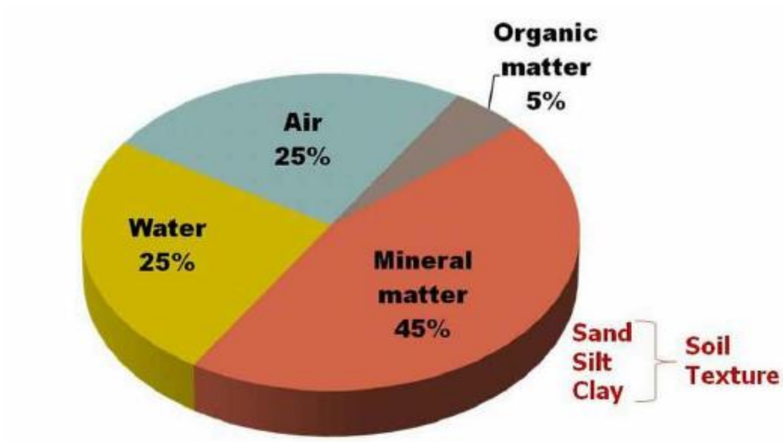
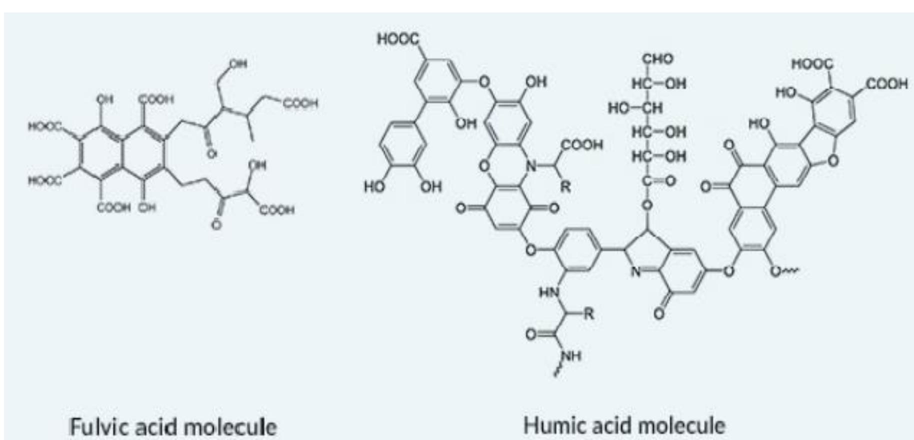


Figure 6. Soil components. Source (Toor et al., 2009).



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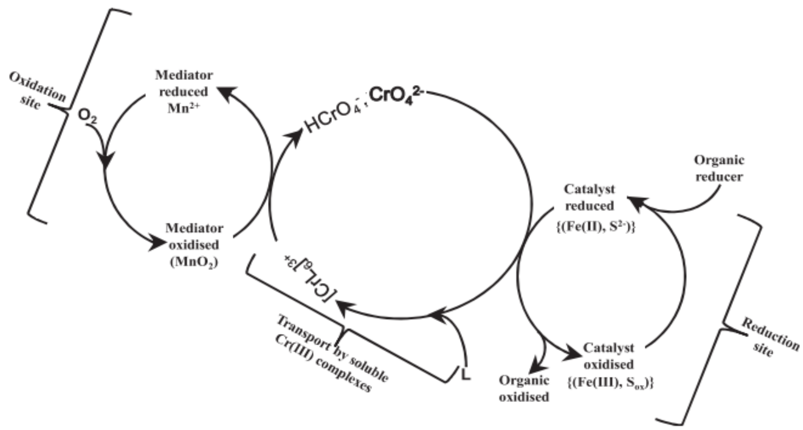
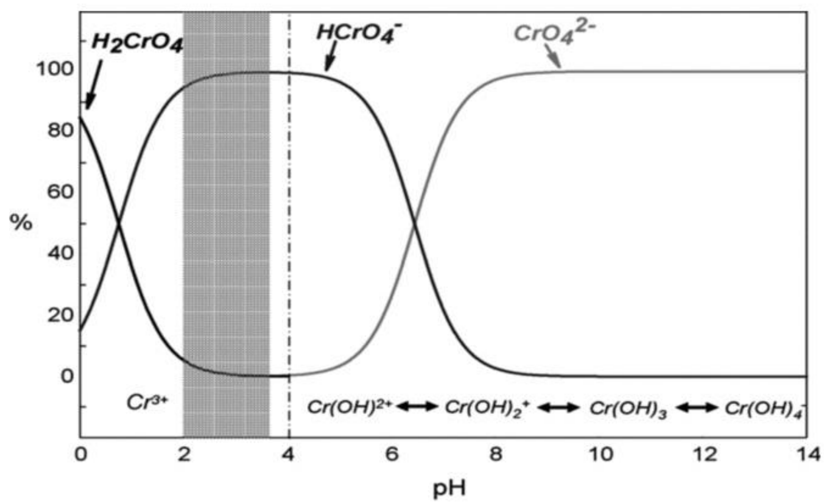


Figure 8. Oxidation/reduction of chromium in soil (Dhal et al., 2013).



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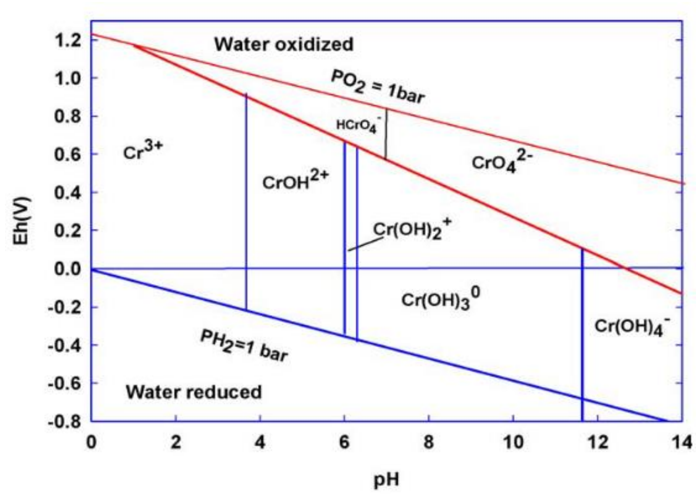

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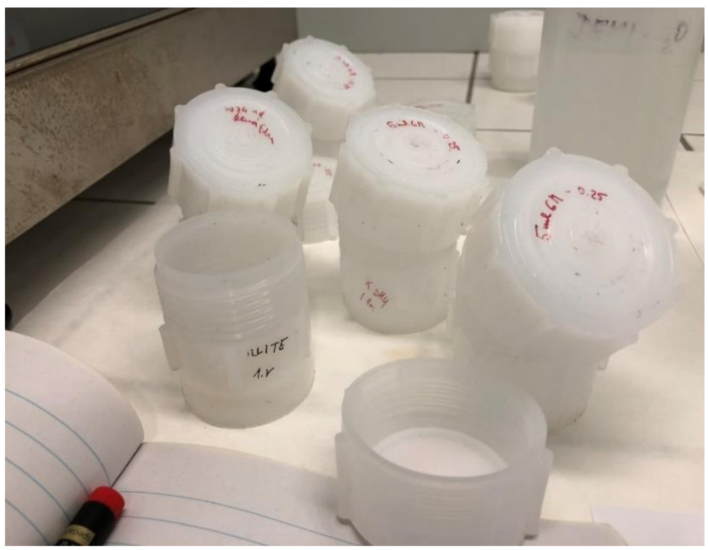


Figure 12. Photo of Savillex digestion Teflons.

Figure 13. Decomposition of humic acids with 2% nitric acid.

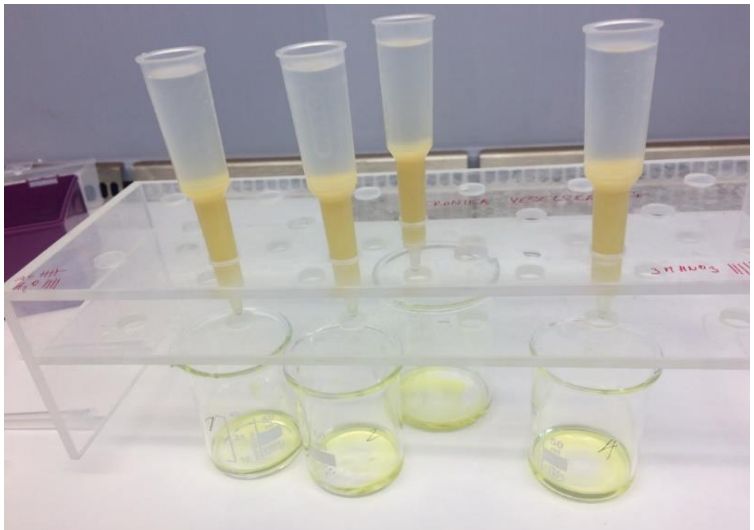


Figure 14. Photo of process of releasing the Fe ions from the columns.

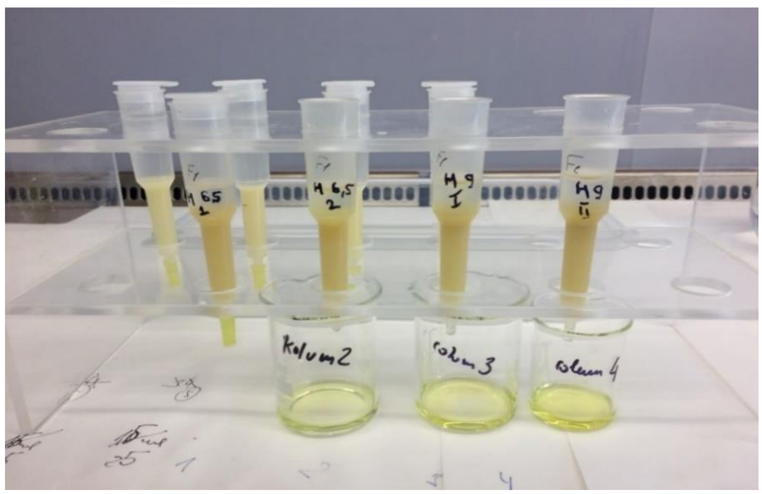
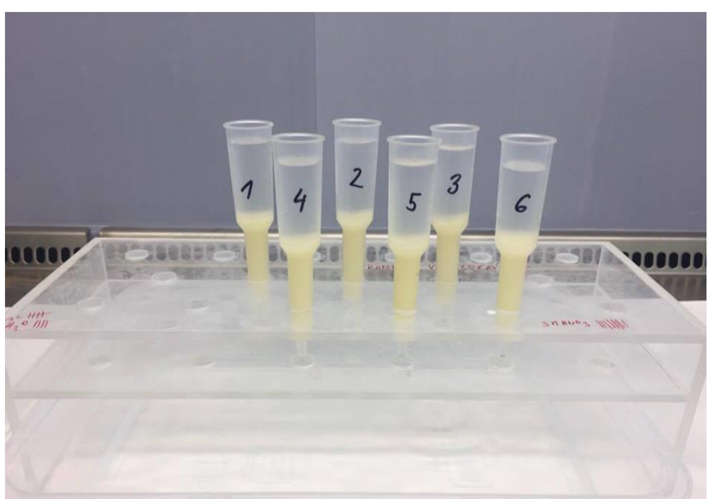


Figure 15. Process of Fe ions released using 0.1M, 10 ml of HCl solution.



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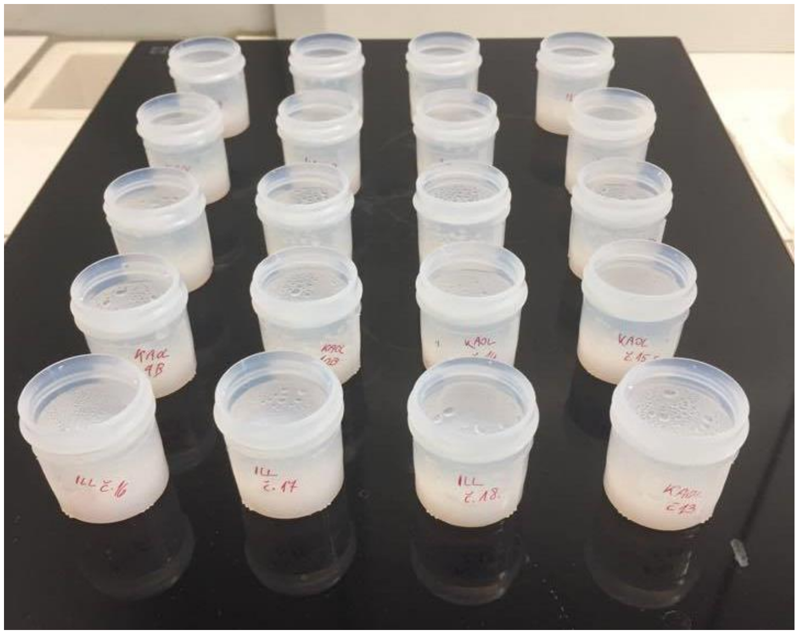

Figure 17. Photo of samples are being evaporated after dissolutiuon in strong acid, ready for further Cr isotope analysis.

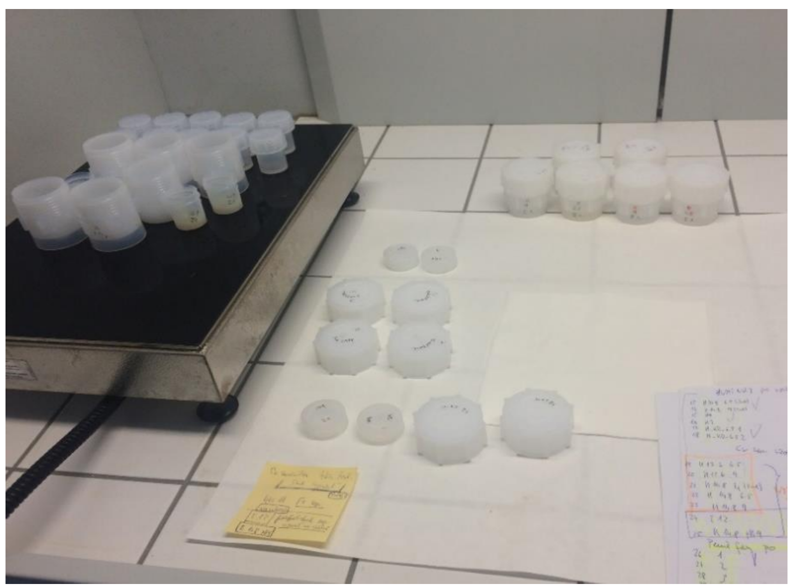

Figure 18. Photo of samples are being evaporated, ready for Cr isotope analysis.

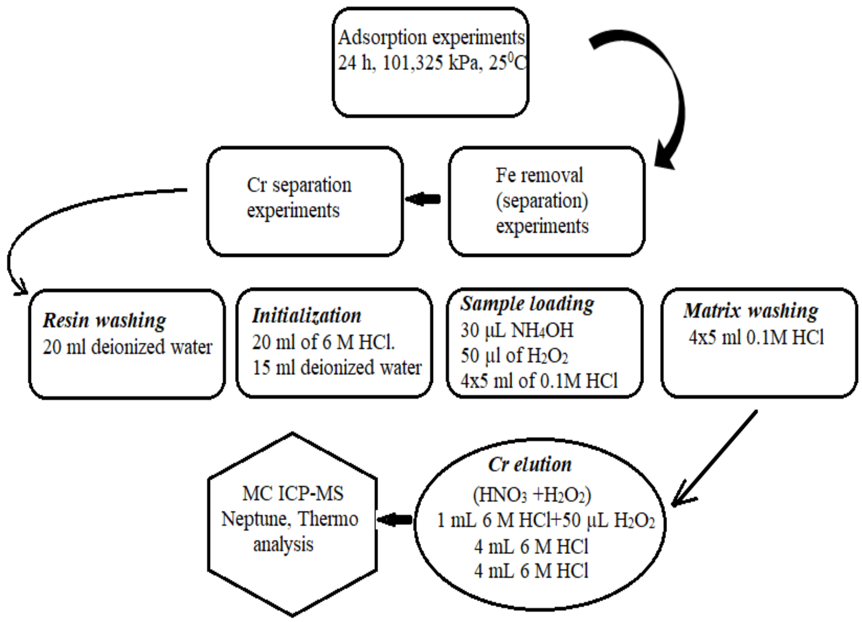

Figure 19. Flow chart of the Cr separation by modified anion exchange chromatography method.

List of tables

Metal	Concentration range mg/kg	Regulatory limit mg/kg
Arsenic	0.1-102	20
Cadmium	0.1-345	100
Chromium	0.005-3950	100
Copper	0.03-1550	600
Mercury	0.001-1800	270
Lead	1-6900	600

Table 1. Heavy metals prevailing in soils (Ahemad, 2015).

Kaolinite	3-18(*meq/100g)
Illite	10-40 (meq/100g)

Table 2. Cation exchange capacities (CEC) of selected clay minerals. (Huggett, 2004).

a. $2(CrO_4)^{2--}+2Fe^{2+}+H_2O+4H^{+}\rightarrow Fe(OH)_3+Cr_2O_3$

b. $(Cr_2O_7)^{2-}+6Fe^{2+}+14H^{+}\rightarrow 2Cr^{3+}+6Fe^{3+}+7H_2O$ (pH<7)

c. $(CrO_4)^{2-}+3Fe^{2+}+4H_2O\rightarrow Cr^{3+}+3Fe^{3+}+8OH$ (pH>7)

d. $3(CrO_4)^{2--}+2FeS+9H_2O\rightarrow 4[Cr_{0.75}, Fe_{0.25}](OH)_3+S_2O_3^{2-}+6OH^{-}$

e. $2(CrO_4)^{2--}+3CaS_4+10OH^{+}\rightarrow Cr(OH)_3+12S^{0}+3Ca+2H_2O$

f. $8(CrO_4)^{2-}3H_2S+10H^{+}\ 4H_2O\rightarrow 8Cr(OH)_3+3SO_4^{2-}$

g. $4(CrO_4)^{2-}{}_{aq}^{-}+6NaHSO_{3\ aq}+3H_2SO_{4\ aq}+8H^{+}_{aq}\rightarrow 2Cr_2(SO_4)_{3\ aq}+3Na_2SO_4^{2-}+10H_2O$

h. $2(CrO_4)^{2-}{}_{aq}^{-}+3SO_{2\ aq}+4H^{+}_{aq}\rightarrow Cr_2(SO_4)_{3\ aq}+2H_2O$

Table 3. Hexavalent chromium involving chemical reduction reactions (Theologou; et al., 2013).

Element	Cr 50 (amu*)	Cr 52 (amu)	Cr 53 (amu)	Cr 54 (amu)
Chromium	4.345%	83.789%	9.501%	2.365%

Table 4. The percentage abundance of stable isotopes of chromium (Moos and Boyle, 2019).

Samples	Initial pH	$\delta^{53}Cr_{init}$ ±2SD	$\delta^{53}Cr_{intri}$ ±2SD	$\delta^{53}Cr_{eq}$ ±2SD	$\Delta^{53/52}Cr_{(lq1-lq2)}$ ‰
Kaolinite	4	-0.475±0020	0.193±0040	-0.217±0081	-0.258
	6.5	-0.475±0020	0.193±0040	-0.209±0056	-0.266
	9	-0.475±0020	0.193±0040	-0.346±0044	-0.129
Illite	4	-0.475±0020	-0.317±0016	-0.398±0004	-0.077
	6.5	-0.475±0020	-0.317±0016	-0.431±0027	-0.044
	9	-0.475±0020	-0.317±0016	-0.632±0075	-0.157
Humic acids	4	-0.475±0020	-0.524±0059	0.039±0066	-0.514
	6.5	-0.475±0020	-0.524±0059	-0.185±0007	-0.29
	9	-0.475±0020	-0.524±0059	-0.210±0038	-0.265

Table 5. Cr isotopic data for the clay minerals and humic acid.

Samples	pH	Initial solution		Intrinsic Cr		Treated solution		Treated solid phase		Mass balance	
		$\delta_1{}^{53}Cr$	m_1 (mg)	$\delta_2{}^{53}Cr$	m_2 (mg)	$\delta_3{}^{53}Cr$	m_3 (mg)	$\delta_4{}^{53}Cr$	m_4 (mg)	Inputs	outputs
Kaolinite	4	-0.475	1.44	0.193	0.19	-0.217	1.00	-1.349	0.29	-0.649	-0.612
	6.5	-0.475	1.44	0.193	0.19	-0.209	0.90	-0.466	0.47	-0.649	-0.409
	9	-0.475	1.44	0.193	0.19	-0.346	1.24	-0.324	0.41	-0.649	-0.561
Illite	4	-0.475	1.44	-0.317	0.20	-0.398	1.19	-0.658	0.17	-0.748	-0.587
	6.5	-0.475	1.44	-0.317	0.20	-0.431	1.22	-0.197	0.32	-0.748	-0.589
	9	-0.475	1.44	-0.317	0.20	-0.632	0.99	-0.225	0.33	-0.748	-0.696
Humic acids	4	-0.475	1.442	-0.524	0.12	0.039	0.35	0.006	0.40	-0.747	-0.016
	6.5	-0.475	1.442	-0.524	0.12	-0.185	0.54	-0.254	0.65	-0.747	-0.266
	9	-0.475	1.442	-0.524	0.12	-0.210	0.60	-0.588	0.25	-0.747	-0.274

Table 6: Data of $\delta^{53}Cr$ values; used for the mass balance calculation.