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Cr(VI) in Soils and Industrial Materials – Geochemistry, Analytical Methods and Case Study

Among inorganic compounds, Cr(VI) is one of the most common and serious contaminants. The highly toxic oxidised form Cr(VI) is mostly released by the galvanic industry, the wood impregnation industry and tanneries where chromic acid (H₂CrO₄) was used. The accumulated Cr(VI) in the subsoil of abandoned industrial sites is constantly washed out and subsequently mobilised by groundwater flowing through the contaminated subsoil. This released Cr(VI) forms a serious threat for drinking water quality, especially in Switzerland where 80% of the drinking water originates from groundwater resources. Another source of Cr(VI) are industrial materials such as cement, fly ash or brick stone. The highly oxidising condition during manufacturing favour oxidation of Cr(III) from the raw material to Cr(VI) in the product, reaching the environment during its use or at the end of its life cycle (disposal).

For assessing the pollution potential at Cr(VI) contaminated sites or of industrial materials, mostly the water-extractable and much more mobile Cr(VI) is determined. The Swiss Ordinance of Waste Disposal (TVA, Swiss Confederation, 1990) and the Contaminated Site Ordinance (AltIV, Swiss Confederation, 1998) ask for extraction methods with deionised water to determine the likely effect of the Cr(VI) contamination to the groundwater. However, there exists no method in legislation to determine the total amount of Cr(VI) in solid materials, and thus the overall potential of Cr(VI) to be released. Most of the Cr(VI) likely occurs in sparingly soluble mineral phases and the Cr(VI) reservoir of a contaminated site is underestimated or unconstrained by just using the standard-TVA tests. Therefore, other extraction and analytical methods are required to determine the total Cr(VI) amount in subsoil and in other solid materials.

This thesis provides a detailed investigation of a method for total Cr(VI) determination. The main goal was the development of a method for a selective and reliable determination of total Cr(VI) in solid samples of different matrix composition. Most commonly, total Cr(VI) is extracted from solid materials following method 3060A, according to the US Environmental Protection Agency (EPA method 3060A, 1996). This method is based on a hot alkaline extraction but has been tested systematically only to a limited degree with respect to compositional differences in the matrix of different Cr(VI) contaminated materials.

The procedure to extract Cr(VI) from various materials was adopted from the original EPA method 3060A (1996), except for the filtration step. Instead of cold filtration as recommended in the EPA method, the extraction solution was filtered in its hot stage. Furthermore, a redox-sensitive analytical method to determine Cr(VI) in the extract solutions was developed. For this reason an ion exchange method (solid phase extraction, SPE) was applied to separate Cr(III) and Cr(VI) prior to ICP-OES quantification. The modified extraction and analytical procedure was then validated on subsoils from the Cr(VI) contaminated Refonda area Niederglatt (ZH), Selve area Thun

(BE) and SBB area Rivera (TI). Furthermore, Cr(VI)-bearing industrial materials such as cements and mortars from Holcim Technology, jetting materials from Theler AG, brick stones from ZZ Wancor and fly ashes from waste incineration plants KEBAG Solothurn and KEZO Zürich were analysed and used for method validation.

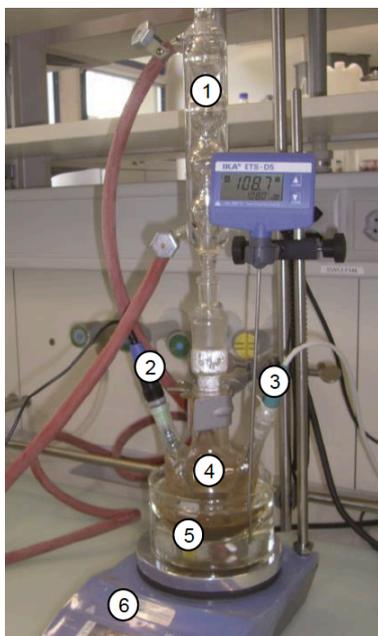
The results of the validation of the modified EPA method 3060A show that the method is not applicable to sample types displaying highly reducing characteristics such as the samples from Rivera. There, weathering products in the subsoil include Cr(VI) reducing agents in the form of ca. 20 wt% Fe(II) bearing minerals. This reducing components cause matrix effects such as Cr(III)-Cr(VI) transitions and cause erroneous results for total Cr(VI) analysis. Therefore, prior to routine application to a new material type, tests are required to identify possible matrix effects occurring during extraction and ICP-OES measurement.

All other tested subsoils and industrial materials showed acceptable results for Cr(VI) obtained by the modified EPA method 3060A. An important observation is that this extraction results in concentrations that are one to two orders of magnitude higher compared to the results according to the standard extraction demanded by the Swiss Ordinance of Waste Disposal (TVA, Swiss Confederation, 1990). The reason for such large discrepancies is that aqueous extractions demanded in Swiss legislation only identify the effect of Cr(VI) contaminated sites to the groundwater whereas results gained by the modified EPA method 3060A provides information about the total Cr(VI) reservoir. Because of the different meaning and interpretation of water-extractable Cr(VI) and total Cr(VI), a representation of both methods is proposed to be included in legislation. It is suggested that the methods for Cr(VI) determination in legislation (TVA, AltIV) should be revised accordingly.

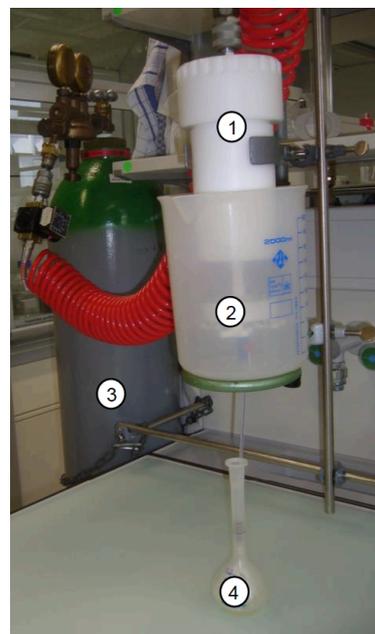
Beside the development, validation and application of the modified EPA method 3060A for total Cr(VI) determination to several contaminated materials, a detailed investigation of the Cr(VI) contaminated Refonda area in Niederglatt was performed. This site was remediated 17 years ago, but still shows elevated Cr(VI) concentrations. The main goal was the determination of the Cr(VI) reservoir and an understanding of the redox processes in the underground. Groundwater and soil samples were collected in two sampling campaigns in 2011 and 2012 and analysed using standard analytical techniques and the modified EPA method 3060A. The analysed groundwater samples taken down-stream of the remediated zone showed Cr(VI) concentrations above the threshold of 0.02 mg/l Cr(VI) according to the Contaminated Site Ordinance (Swiss Confederation, 1998). North of the remediated zone, the existence of large amounts of Cr(VI) in the subsoil could be shown. In general a portion of ca. 4% of Cr(tot) was found to be present as Cr(VI) in the soil material of the Refonda area. Evidence for oxidation processes of dissolved Cr(III) to Cr(VI) facilitated by Mn(IV) could not be proven and such a redox

reaction under natural conditions without the addition of Cr(III) in solution cannot be expected. Therefore, mobilisation due to oxidising processes in the remediated zone can be excluded at this specific site in Niederglatt. Therefore, the measured Cr(VI)

concentrations in the groundwater originate with high probability from non-remediated subsoil parts located in the north of the remediated zone.



1. Reflux condenser or watch glass
2. Eh electrode (optional)
3. pH electrode (optional)
4. 250 ml round bottom flask
5. Oil bath
6. Magnetic stirrer with heating device



1. Teflon pressure vessel with coarse filter (40 µm) on the bottom
2. Fine filter (0.8 µm)
3. Ar-gas bottle
4. 100 ml volumetric flask

Extraction device

Pressure filtration device



Refonda area at Niederglatt 2007 (Gerber et al., 2007).



Core N01 with dark brown parts which are heavily contaminated on the left side (N01-2a) and brighter, sandier parts on the right side (N01-2b).

Gerber, J., Huber, J., & Reinli, H. (2007). Die Fabrik: Knapp hundert Jahre Industriegeschichte in Niederglatt. Im Wandel der Zeit - Metallwerke Refonda AG - Die Fabrik (pp. 1–283). Alcan - Metallwerke Refonda AG, Niederglatt.