Molybdate adsorption from steel slag eluates by subsoils

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HIGHLIGHTS

- Molybdate adsorption from steel slag eluates was evaluated.
- Steel slag eluates were used as a background electrolyte.
- Molybdate transport simulations revealed a small discharge into the groundwater.
- Acid soils decreased the eluate pH favouring molybdate adsorption.

ARTICLE INFO

ABSTRACT

Steel slags are industrial by-products which are generated in large amounts worldwide, e.g. 150–230 × 10^6 Mg in 2012, and which are partly used for construction. Molybdenum (Mo) can be added during steel processing in order to harden the steel. The objective of this study was to evaluate the adsorption behaviour of molybdate (MoO_4^{2-}) from slag eluates in subsoils. Molybdate batch adsorption experiments were carried out with eluates obtained from two different kinds of steel slags (i) LD slag (Linz-Donawitz operation, LDS) and (ii) electric arc furnace slag (EAF) to assess the risk that may arise from the contamination of groundwater by the leaching of molybdate. Six different subsoils were chosen in order to provide a wide range of chemical properties (pH 4.0–7.6; dithionite-extractable Fe 0.73–14.7 g kg^{-1}). Molybdate adsorption experiments were carried out at the pH of the steel slag eluates (pH 11–12) as well as at pH values adjusted to the soil pH. The data were evaluated with the Freundlich equation. Molybdate adsorption exhibited a maximum near pH 4 for steel slag eluates adjusted to the soil pH, and decreased rapidly with increasing pH until adsorption was virtually zero at pH > 11. Adsorption was greater for soils with high amounts of dithionite-extractable Fe oxides. The extent and behaviour of molybdate adsorption from both eluates was similar. After a reaction time of 24 h, the pH of the EAF slag eluate was lower than that of the LD steel slag eluate, which was caused by different acid buffer capacities. Some soils were able to decrease the pH of the EAF slag eluates by about 4 pH units, enhancing the adsorption of molybdate. Transport simulations indicated that molybdate discharge is low in acidic soils.

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1. Introduction

Large quantities of steel slag are utilised worldwide as a construction material. The global production of steel slag in 2012 is estimated to 150–230 × 10^6 Mg (U.S. Geological Survey, 2013). The amount of steel slag generated in the European countries is about 21.8 × 10^6 Mg in 2010 from which 48% was used as a construction material for paths, roads and earthworks (Euroslag, 2012). The use of slag as a construction material has been well examined and has a long tradition (Geiseler, 1996; Motz and Geiseler, 2001; Zhang and Hong, 2011). Whether such slag can be used in civil engineering projects is, apart from its technical

suitability, determined by environmental compatibility, including the leachability of environmentally relevant elements. The solubility of major elements (Ca, Mg, Fe, Si, Al) and some minor elements (Cr, Mo, V) has been investigated (Fällman, 2000; Bialucha, 2007; Chaurand et al., 2007; Tossavainen et al., 2007; Cornelis et al., 2008; De Windt et al., 2011), but information on the adsorption of these elements in soil constituents after their release from slags used for road construction is still lacking.

Molybdenum (Mo), can be used as alloying element in steel production (especially high alloy steel) – e.g. in order to increase the wear resistance. Molybdenum is charged into the material vessels by alloying additives (e.g. ferro molybdenum) or alloyed scrap. Molybdenum is an essential trace element for plants, animals and humans (Gupta, 1997). Whereas most plants and humans are insensitive to high Mo concentrations, ruminants develop molybdenosis, a Mo induced copper deficiency (Underwood,

1976). Kubota et al. (1967) suggested that the consumption of forage containing 10–20 mg kg^{-1} Mo by grazing animals leads to this disease. However, the National Research Council (1984) indicates a level of 6 mg kg^{-1} Mo for cows. Although toxic effects in humans do not occur, WHO (2011) determined a health-based reference value of 70 $\mu g \, L^{-1}$ Mo for drinking water. Therefore, the use of steel slag with a non negligible leaching of molybdenum which may end up in the groundwater must be carefully managed. Consequently, detailed knowledge of the extent of Mo retention in soils is required, being one of the most important media for the distribution and availability of Mo in the environment.

The molybdenum component contained in slags forms molybdate (MoO_4^{2-}), an oxyanion, following release in the alkaline milieu of the slag eluates. Referring to speciation diagrams (Lindsay, 1979), $HMoO_4^-$ and $H_2MoO_4^0$ can also occur in solution in the pH range of 3–5, but according to Lindsay (1979) MoO_4^{2-} is the dominant Mo species in solution with pH > 4.24. For simplicity, we summarise all Mo species as molybdate (MoO_4^{2-}) in the following. Molybdate adsorption in soils depends on the pH, ionic strength, Mo concentration, concentration of competitive anions, temperature, time and soil mineralogy (Barrow, 1970; Barrow and Shaw, 1975; Barrow 1989; Xie and Mackenzie, 1991; Xie et al., 1993; Goldberg and Forster, 1998; Lang et al., 2000; Goldberg et al., 2002; Lang and Kaupenjohann, 2003; Goldberg et al., 2008; Saeki, 2008; Arai, 2010; Goldberg, 2010). Molybdate is adsorbed by various mechanisms by the soil components. The major mechanism of molybdate adsorption onto the surface of Fe and Al oxides is ligand exchange with surface hydroxyls forming an inner-sphere surface complex (Ferreiro et al., 1985; Peng and Sparks, 1989; Bibak and Borggard, 1994; Goldberg et al., 1996). Goldberg et al. (1996) stated that molybdate adsorption by oxides also occurs as outer-sphere complexation at an increasing solution pH.

The extent of molybdate adsorption is highly correlated with pH, with a maximum near pH 4 derived from adsorption envelopes (Hingston et al., 1967, 1972). The adsorption maximum is close to the pK_a of the conjugate acid (molybdic acid with pK_{a1} = 4.00 and pK_{a2} = 4.24; Lindsay 1979) and rapidly decreases with increasing pH.

The major mechanism of molybdate adsorption in clay minerals is also inner-sphere surface complexation (Goldberg et al., 1996) with the same pH dependency and virtually no adsorption at pH 7. Molybdate adsorption increases in the following order: well-crystalline kaolinite < poorly crystalline kaolinite < illite < montmorillonite (Goldberg et al., 1996). Overall, molybdate adsorption by clay minerals is lower than adsorption by Fe and Al oxides (Goldberg and Forster, 1998).

The aim of this study was to determine the long term adsorption behaviour of molybdate from steel slag eluates in order to assess potential groundwater contamination by molybdate. The slags used in the current study were a Linz–Donawitz (LD) slag from a basic oxygen steelmaking process and an electric arc furnace (EAF) slag from the melting of scrap in an electric arc furnace. Both types of slag have different properties (pH, chemical and mineralogical composition) resulting from the different production processes. Both slags are calciumsilicatic. The main differences in the mineralogical composition are the higher contents of CaO (420–550 g kg^{-1}) and CaO$_{free}$ (10–100 g kg^{-1}) of the LD slag in contrast to the EAF slag with a content of CaO (250–400 g kg^{-1}) and CaO$_{free}$ (10–30 g kg^{-1}) (Motz and Geiseler, 2001), that react in contact to water to calcium hydroxide. Indeed molybdate adsorption has been investigated on a wide range of soils and soil constituents. A major innovation of this research was the experimental design with steel slag eluates as the background electrolytes, which may have a significant influence on adsorption due to their specific chemical composition. Adsorption parameters derived from Freundlich isotherms were used to simulate the

transport of molybdate, which we assume to be continuously released from the deposited steel slag, through the soils to assess its potential export into the groundwater over 200 years.

2. Materials and methods

2.1. Sampling sites and sample preparation

Molybdate adsorption was investigated with 4 strongly weathered (B horizons; #1, #3, #4, #6) and two weakly weathered subsoil horizons (C horizons; #2, #5), which were chosen to provide a wide range of soil chemical characteristics. The samples were taken from sites in Germany close to Diez, Rhineland-Palatinate (#1 and #4), Cologne (#2 and #5) and Rheine (#6) in North Rhine-Westphalia and Haselünne (#3) in Lower Saxony. Sampling was restricted to the subsurface soil, because humus-rich topsoils are removed before path construction. The samples were manually homogenised, air dried and sieved to <2 mm.

2.2. Characterisation of the samples

Particle-size distribution was analysed by wet sieving and sedimentation using the pipette sampling technique. Prior to such analyses, soil organic matter was destroyed with H_2O_2 (#2, #3, #4), and carbonates were destroyed with HCl (#2, #4, #5). Soil pH was measured potentiometrically using a glass electrode (Sen TIX 81, WTW Wissenschaftliche-Technische Werkstätten) in 0.01 M $CaCl_2$ extracts with a soil:solution ratio of 1:5. Contents of oxalate-extractable Fe (Fe_o) were determined according to Schwertmann (1964) and dithionite-citrate extractable Fe (Fe_d) according to Mehra and Jackson (1960). Total C was quantified with an elemental analyzer (Vario EL, Elementar). Samples with pH $\geqslant$ 6.5 (#2, #4) were additionally analysed for inorganic C with the same equipment by adding 10% HCl to the weighed samples. Inorganic C was calculated from the difference between the total and organic C, which remained after the application of HCl. Total C equals organic C when the sample is free of carbonates. The content of phosphate-extractable molybdate was determined by inductive coupled plasma mass spectrometry (ICP-MS, X-Series II, Thermo Scientific) in 0.01 M K_2HPO_4 with a soil:solution ratio of 1:5, using a modified method of Fox et al. (1964). The content of phosphate-extractable sulphate was determined by ion chromatography (ICS-1000, Dionex) in 0.01 M K_2HPO_4 with a soil:solution ratio of 1:5 (Fox et al., 1964). Plant-available phosphate was measured spectrophotometrically at 580 nm using a UV/Vis Spectrometer (Lambda 25, Perkin Elmer) in a calcium–acetate–lactate (CAL) solution with a soil:solution ratio of 1:20. Exchangeable acidity was determined in 1 M KCl with a soil:solution ratio of 1:10 according to Rowell (1997). Total exchangeable acidity was determined by titration with a 0.01 M NaOH, and the content of exchangeable Al was measured by ICP-MS. The content of protons was calculated from the difference between the total acidity and exchangeable Al.

2.3. Preparation and characterisation of the steel slag eluates

Two different slags, one from LD operations and one EAF slag, obtained from steelworks in Germany were leached by shaking for 24 h at a demineralised-water:slag ratio of 2:1 at the FEhS Institute (Institut für Baustoff-Forschung e.V., Duisburg, Germany; Sokol et al., 2011). Both slags were grained <5 mm. The eluate pH was measured potentiometrically as previously mentioned. The electric conductivity was determined using a conductivity electrode (SevenEasy, Mettler-Toledo), and the ionic strength (I)