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Cr(VI)-LEACHING FROM LANDFILLED STEEL PROCESSING SLUDGE AS DRIVEN BY ENHANCED NITRITE OXIDATION

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ABSTRACT

Pickling with hydrofluoric and nitric acid is a common treatment to remove oxide scales from hot-rolled stainless steel. Acid residues at the steel surface are eliminated by rinsing with water. The rinse water exhibits high concentrations of metals {Cr(III), Ni(II), Fe(III)} and nitrite (NO_2^-) from the oxide scales and pickling acids, respectively which are typically removed by the following steps: (i) oxidation of NO_2^- by hydrogen peroxide (H_2O_2), (ii) precipitation of metal hydroxides by lime milk and (iii) solid-liquid separation by settling and filtration. The additive H_2O_2-dosage is experience-based and does not account for the temporal variability of pollutant levels (e.g. NO_2-N concentrations between <0.05 and 75 mg/L as evidenced during a screening campaign). Whereas the purified water may discharged to tributary the resulting steel processing hydroxide sludge (SPHS) is landfilled.

This study focused on the causes of chromate [Cr(VI)] concentrations of 5 to 20 mg/L observed in the seepage water of a SPHS mono-landfill section. Chromate incidence was unexpected since the waste water contains Cr(III) exclusively and no Cr(VI) was present in the batch leachates conducted to prove conformity with the waste acceptance criteria (WAC). Against the background of the pH-dependent oxidation/reduction of Cr by H_2O_2 the water treatment process was downscaled to laboratory conditions. Generation of SPHS was performed continuously stirred tank reactor. Rinse water, collected at the steel processing plant, was reacted according to the water treatment train outlined above. Analysis of dissolved Cr(VI) was carried out colourimetrically standard 1,5-diphenyl-carbohydrazide method. For the extraction of Cr(VI) possibly adsorbed on the SPHS, phosphate was used as a competing anion. The produced SPHS was subjected to a sequential batch leaching procedure on an orbital shaker for a total of 20 days to mimic the time dependent processes in the landfill body.

Compared to a control without nitrite oxidation, H_2O_2 addition to the rinse water caused a significant Cr(VI)-release from the precipitated sludge. The H_2O_2-amended sludge exhibited a continuous release of both dissolved and adsorbed Cr(VI). Adsorbed Cr(VI) levels were several orders of magnitude higher than dissolved Cr(VI) indicating a high affinity of Cr(VI) to specific surface sites of the metal hydroxides. This may hamper the recognition of the true leaching potential by the standardized leaching protocols employed in WAC testing. The release of Cr(VI) was minimal at the maximum initial level of NO_2^-, since a carry-over of excess H_2O_2 to the alkaline metal precipitation step was avoided.

Overall, our results strongly corroborate the hypothesis that the incidence of Cr(VI) in the seepage water of a SPHS mono-landfill section is related to the enhanced NO_2-oxidation of steel processing effluents. This is supported by the high variability of NO_2 concentration in the rinse water in combination with the risk of excess H_2O_2 dosage which promotes Cr(III) oxidation under alkaline conditions.

Keywords: Chromate, nitrite, hydrogen peroxide, advanced oxidation, hazardous waste

1. Introduction

Exhausted process waters of the steel processing industry (rinse water) exhibit high concentrations of metals {Cr(III), Ni(II), Fe(III)} and nitric and hydrofluoric acids (Gálvez *et al.*,

2009). Additionally, also high levels of nitrite (NO_2^-), originating from the reaction between oxide scales and pickling acids, are found in the steel process waters).

Rinse water treatment typically involves an enhanced NO_2-oxidation followed by the precipitation of metals, mainly as metal(hydr)oxides, via addition of lime milk {$Ca(OH)_2$}. While the purified water may be discharged into a tributary when complying with legal limits the resulting steel processing hydroxide sludge (SPHS) is dewatered and finally landfilled on a hazardous waste landfill section (see Fig. 1).
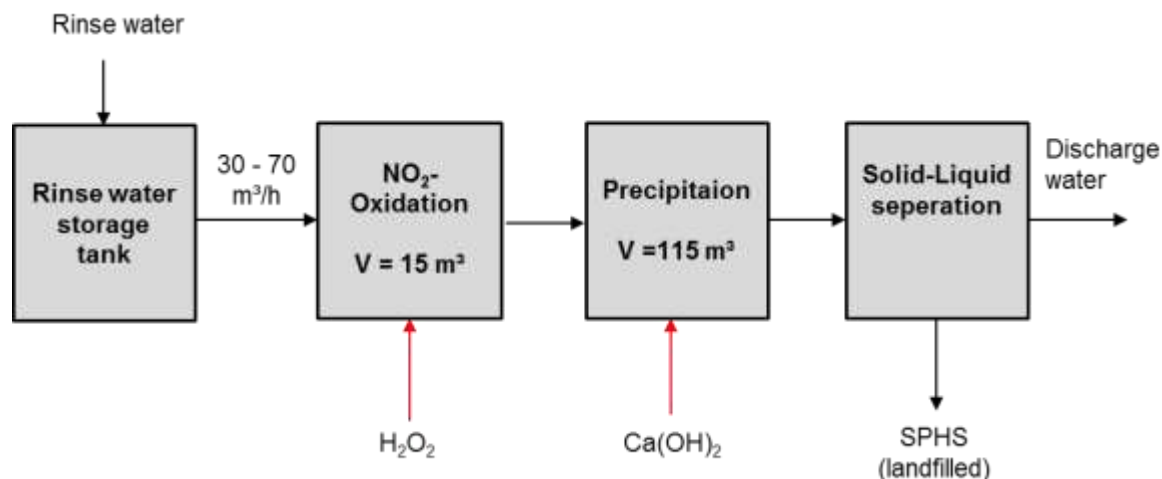

Figure 1: Flow diagram of the treatment train. Red arrows indicate reagent streams.

Hydrogen peroxide (H_2O_2) is one of the most commonly used oxidants for NO_2^- elimination from process waters (Förtsch and Meinholz, 2014). It is still common practice in the steel manufacturing industry, even though problems related to Cr(III) oxidation have been pointed out by several authors (Fabjan and Bauer, 1976; Trunfio and Crini, 2010).

The complex chemistry of H_2O_2 and chromium involves ligand exchange, proton transfer, oligimerization and redox reactions (Ranganathan *et al.*, 1989). Broadly speaking, the fate of the H_2O_2-triggered redox reactions is determined by the pH of the solution. At pH < 2 Cr(VI) quickly reacts to the unstable blue peroxochromic acid which then is reduced to Cr(III) (Pettine *et al.*, 2002). A similar reaction is observed at slightly acidic pH (2 to 7), but instead of the blue peroxochromic intermediate a violet intermediate occurs (Witt and Hayes, 1982). The latter is partially regenerated to Cr(VI) by intramolecular peroxide disproportionation and only a limited fraction is finally reduced to Cr(III) (Perez-Benito and Arias, 1997). At slightly to moderately pH H_2O_2 oxidizes Cr(III) to Cr(VI).

This study focused on the causes of Cr(VI) concentrations of 5 to 20 mg/L observed in the seepage water of a SPHS mono-landfill. Chromate incidence was unexpected since the waste water contains Cr(III) exclusively and no Cr(VI) was present in the batch leachates conducted to prove conformity with the waste acceptance criteria (WAC). Against the background of the pH-dependent behavior of Cr the treatment was downscaled to lab conditions. The SPHS was generated from rinse water either with or without H_2O_2 treatment.

2. Materials and methods

Lab-scale generation of SPHS was performed in a continuously stirred tank reactor (CSTR) with a void volume of 10 L. All experiments were performed under ambient conditions. The CSTR was equipped with several electrodes (pH, ORP and electrical conductivity). The rinse water from a steel processing plant was reacted according to the water treatment train outlined in Figure 1. First, a defined quantity of H_2O_2 was added. After 15 minutes the pH was raised to 10

by adding a Ca(OH)$_2$ suspension. After 30 minutes the CSTR was stopped and the suspension was allowed to settle (sediment volume ~ 1L) for 45 minutes. The pH, ORP, and electrical conductivity (EC) were logged during the experiment. Sample aliquots (25 mL) were taken from the upper part from the CSTR and immediately analysed for dissolved and adsorbed Cr(VI).

For the determination of Cr(VI) adsorbed on the SPHS, the suspension was treated as follows: an aliquot of 25 mL was mixed with 25 mL distilled water and 0.5 mL of phosphate-buffer (K$_2$HPO$_4$, 2 M, pH: 9.0) were added. The resulting pH was between 7.5 and 8.0. Pechenyuk *et al.* (2013) demonstrated that phosphate at equimolar concentrations completely displaces adsorbed Cr(VI) from oxy(hydr)oxide surfaces. In our case, preliminary tests showed that maximum Cr(VI) desorption (< 0.04 mM) was achieved with phosphate at a concentration of 1 mM. After 10 minutes of settling the suspension was centrifuged for 5 Minutes at 3000 rpm. Analysis of dissolved Cr(VI) was then carried out colorimetrically using the 1,5-diphenyl-carbohydrazide method. Concentrations of Cr-, Ni- and Fe-tot were analysed by atomic absorption spectrometry (AAnalyst 100, Perkin Elmer). Analysis of nitrite (NO$_2^-$) was conducted using the colorimetrical Hach method LCK 341.

3. Results and discussion
3.1. General chemical characterization of the rinse water
Rinse water samples from the steel processing plant were monitored from May 2012 through December 2013. Table 1 summarises the results. Dominant constituents of exhausted rinse water are Fe, Cr and Ni as well as nitrate and fluoride. The concentration of the individual pollutants covers a broad range, e.g. NO$_2^-$ concentrations between <0.05 and 75 mg/L whereas 1.9 mg/L were found in the sample used for our experimental work. This variability may be related to changing pickling bath operation, which however is not accounted for in the H$_2$O$_2$ dosage. Hence there is a strong likelihood for H$_2$O$_2$ excess and carryover to the alkaline process steps.

Table 1 - Analysis of rinse water.

Parameter	Sample	Typical range		
pH (-)	2.3	1.9	-	4.0
Eh (mV)	864	700	-	900
EC (mS/cm)	18.6	4.0	-	20.0
Cr-tot (mg/L)	87	30	-	100
Cr(VI) (mg/L)	0.05	<0.01	-	0.070
Ni-tot (mg/L)	71	30	-	90
Fe-tot (mg/L)	430	150	-	700
F$^-$ (mg/L)	872	400	-	1000
NO$_3^-$ (mg/L)	4560	1800	-	5000
NO$_2^-$ (mg/L)	1.9	<0.05	-	75

3.2. Cr(VI)-formation during rinse water treatment
Against the background of the pH-dependent oxidation/reduction of Cr by H$_2$O$_2$ the water treatment process was downscaled to laboratory conditions. Figure 2a depicts the temporal course of Cr(VI) during rinse water treatment. Upon Ca(OH)$_2$-addition the concentration of dissolved and adsorbed Cr(VI) increased rapidly. Obviously, the formed Cr(VI) showed a high affinity to the surface of the freshly precipitated metal hydroxides. Thus, the concentration of adsorbed Cr(VI) dropped after the start of the sedimentation (samples taken from the 'supernatant'). After 24 h concentration differences of the Cr(VI) fractions levelled-out. In case of excess H$_2$O$_2$ from the NO$_2$-elimination step, adsorption of Cr(VI) is a likely pathway for the transfer of high amounts of Cr into the sludge. Figure 2c shows that the formation of dissolved Cr(VI) depends on the initial NO$_2$-level. Anti-correlation of Cr(VI) and NO$_2$ may indicate that H$_2$O$_2$ is almost entirely consumed for the oxidation of NO$_2^-$. Thus, carryover of H$_2$O$_2$ into the alkaline precipitation step is triggered in the absence of NO$_2^-$.
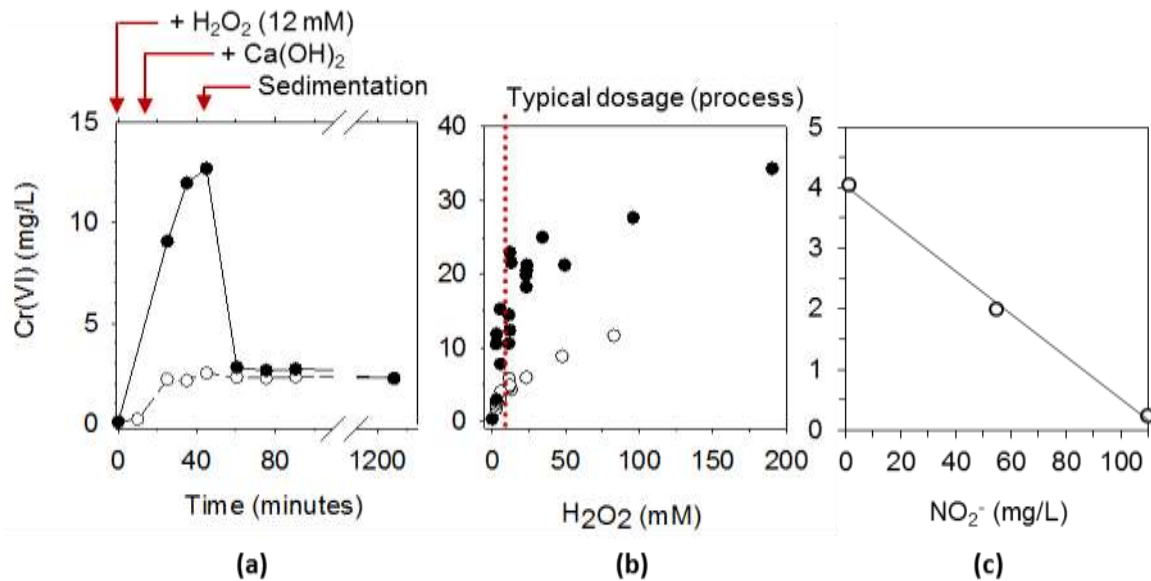
Figure 2: Formation of Cr(VI) a) during rinse water treatment in the CSTR; b) at varied H_2O_2 dosage; c) at varied NO_2^- concentration. Symbols: Cr(VI) diss. (○); Cr(VI)-tot. (●).

3.3. SPHS-leaching tests

To mimic the time-dependent processes in the landfill body, the experimentally-derived SPHS was sequentially leached under batch conditions for 19 days. This involved SPHS produced in the absence and presence of H_2O_2. Figure 3 documents the temporal evolution of dissolved and adsorbed Cr(VI). In the H_2O_2 treatment a strong release of dissolved and adsorbed Cr(VI) was observed. Especially during the first 5 to 7 days a rapid increase occurred. Adsorbed Cr(VI) levels were several orders of magnitude higher than dissolved Cr(VI), throughout. This is consistent with the observations from the water treatment experiment (see Fig. 2 a, b). The liquid to solid ratios tested here were way above the standard of 10 to 1 (i. e. more dilute). Thus, concentrations are not directly comparable with the WAC for Cr(VI). The large proportion of adsorbed Cr(VI) points to the fact that the standard leaching protocol is not suited to forecast the behaviour of the sludge under landfill conditions.
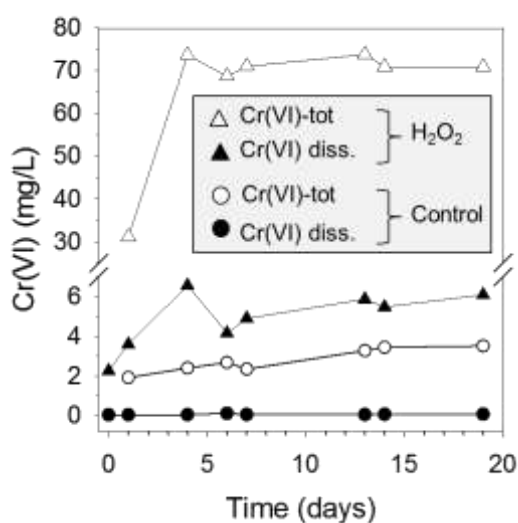

Figure 3: Time-dependent release of dissolved and adsorbed Cr(VI) in SPHS-suspensions generated without H_2O_2-treatment (control) and with 60 mM H_2O_2.

4. Conclusions

Our results strongly corroborate the hypothesis that the incidence of Cr(VI) in the seepage water of a SPHS mono-landfill section is related to the enhanced NO_2-oxidation of steel processing effluents using H_2O_2. This is supported by (i) the high variability of NO_2^- concentration in the rinse water linked to the risk of H_2O_2 overdosage and (ii) the high Cr(VI) concentrations observed in H_2O_2-treatments undergoing the alkaline process step. Both, the lab-scale water treatment and the SPHS-leaching tests showed that the main fraction of Cr(VI) was adsorbed to the SPHS and could be desorbed using phosphate as a competing anion.

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