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Leaching of hexavalent chromium from young chromite ore processing residue

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Abstract

Chromite ore processing residue (COPR) is a waste derived from the chromate extraction from roasted ores and is deposited in some countries in landfills. The objective of this study was to investigate the leaching characteristics of hexavalent Cr [Cr(VI)] from two COPR samples obtained from unlined landfills in the Kanpur area of northern India. Column experiments were conducted under water-saturated conditions to simulate Cr release from the wastes caused by tropical heavy-rain events. Leached Cr(VI) decreased from 1,800 to 300 mg L^{-1} (Rania site) and 1,200 to 163 mg L^{-1} (Chhiwali site) during exchange of 12 pore volumes, which approximately corresponds to 2 yr of monsoon precipitation. Flow interruptions for 10, 100, and 1,000 h had little effect on Cr(VI) concentrations in the leachate, suggesting that Cr(VI) leaching was not limited by slow release kinetics. Calcium aluminum chromium oxide hydrates (CAC), and highly soluble phases such as Na_2CrO_4 may play a role in controlling Cr(VI) concentration in the leachates. The amount of Cr(VI) leached from the columns accounted for 16% of the total Cr(VI) present in both COPR samples. A decrease in the solid-phase Cr(VI)/Cr$_{total}$ ratio along the column was identified by X-ray absorption near edge structure (XANES) spectroscopy. Consistently, the smallest Cr(VI)/Cr$_{total}$ ratios were found in the lower column section closest to the inflow. Our results suggest that Cr(VI) leaching from the unlined COPR landfills will continue for centuries, highlighting the urgent need to remediate these dumpsites.

1 | INTRODUCTION

High amounts of chromite ore processing residue (COPR) have been deposited in the environment in numerous indus-

trial regions worldwide. The material is a hazardous waste derived from the extraction of chromate (CrO_4^{2-}) from ground and roasted chromite ores. In the roasting process, insoluble trivalent chromium [Cr(III)] present in the ores oxidizes to soluble hexavalent Cr [Cr(VI)], which is then recovered by aqueous leaching for further processing (Burke et al., 1991). The technology dates back to 1845 and is still in use in some emerging economies such as Russia (Sokol, Nigmatulina, & Nokhrin, 2010), Kazakhstan (Sokol et al., 2010), Pakistan (Darrie, 2001), India (Matern, Weigand, Singh, &

Abbreviations: CAC, calcium aluminum chromium oxide hydrate(s); COPR, chromite ore processing residue(s); ICP–OES, inductively coupled plasma optical emission spectrometry; PV, pore volume(s); SEM, scanning electron microscopy; XANES, X-ray absorption near edge structure; XRD, X-ray powder diffraction.

Mansfeldt, 2017), and China, whereby China also has used soda ash instead of lime since 2013 (Du & Chrysochoou, 2018).

Chromite ore processing residue contains unreacted chromite ore as well as residual (i.e., nonextracted) CrO_4^{2-}. In general, COPR is strongly alkaline, with pH values typically between 11.0 and 12.5 (Chrysochoou, Fakra, Marcus, Moon, & Dermatas, 2009; Deakin, West, Stewart, & Yardley, 2001b; Földi, Dohrmann, Matern, & Mansfeldt, 2013). Residual Cr contents of COPR range from 20 to 100 g kg^{-1} (Farmer et al., 1999; Földi et al., 2013; Geelhoed et al., 2003), where the majority of Cr is present as Cr(III) in unreacted chromite, but Cr(VI) can also be present in levels of up to 30% (Geelhoed et al., 2003).

The two oxidation states differ in their chemical properties, environmental behavior, and toxicity. Whereas Cr(III) is relatively immobile in most environmental systems (Fendorf, 1995), Cr(VI) is highly soluble and mobile in soils, particularly under slightly acidic to moderately alkaline conditions (Matern & Mansfeldt, 2016a). Hexavalent Cr [Cr(VI)] is a well-known human lung carcinogen (Halasova et al., 2009; Holmes, Wise, & Wise, 2008), has carcinogenic potential by oral exposure (Sun, Brocato, & Costa, 2015), and causes allergic contact dermatitis (Shelnutt, Goad, & Belsito, 2007). In contrast, Cr(III) is an essential dietary micronutrient according to today's knowledge (Pechova & Pavlata, 2007).

After landfilling, COPR is not stable and undergoes weathering reactions resulting in destabilization and dissolution of Cr(VI)-bearing minerals (Chrysochoou, Dermatas, Grubb, Moon, & Christodoulatos, 2010; Geelhoed et al., 2002; Wazne, Jagupilla, Moon, Christodoulatos, & Koutsospyros, 2008). One consequence are elevated Cr(VI) concentrations in ground and surface water at COPR-affected sites, which may even be visually discernible by the characteristic yellow stain (Farmer et al., 2002; Matern et al., 2017).

This study focuses on two sites near Kanpur (Uttar Pradesh, northern India), where COPR from local chromite ore processing plants was landfilled under uncontrolled conditions. The first site is located in Rania in the district of Kanpur Dehat, west of Kanpur. Here, a plant was in operation from the late 1980s until 2005. The thereof-derived COPR heap covers an area of ~1 km^2, is several meters thick, and contains ~30,000 Mg of waste (Jaiswal & Braun, 2010). The second site is located in Chhiwali in the district of Fatehpur, southeast of Kanpur. Here, two Cr works were established in 2004 and are currently still operating.

The Cr(VI) contamination related to the dumpsites is evident from a variety of investigations. Concentrations of Cr(VI) up to 80 mg L^{-1} were found in piezometers close to the main dumpsite in Rania (Singh, Sachan, Ansari, Pandey, & Kamyotra, 2013). Aside from groundwater contamination, there is a risk of migration of Cr(VI) and contamina-

Core Ideas
- Hexavalent Cr [Cr(VI)] was highly mobile in the chromite ore processing residue.
- Response to flow interruptions indicated equilibrium between solid and solution phases.
- Ratio of Cr(VI)/Cr$_{total}$ decreased during column experiments.

tion of nearby soils, which are predominantly under agricultural use. Matern and Mansfeldt (2016b) reported a Cr content of 0.54 g kg^{-1} in an agricultural field close to a COPR dumpsite, where ~9% of the Cr was present in the mobile or exchangeable form.

Although leaching of Cr(VI) from soils (Andjelkovic et al., 2012; Matern & Mansfeldt, 2016b; Weng, Huang, Allen, Cheng, & Sanders, 1994) and COPR (Deakin, West, Stewart, & Yardley, 2001a, 2001b; Geelhoed et al., 2002; Wazne et al., 2008; Yalcin & Ünlü, 2006) has been widely studied, the findings cannot be simply transferred to the Indian sites. This is due to the fact that COPR mineralogy differs depending on (a) chromite ore composition, (b) the extraction process (especially the complexing agent), (c) landfilling conditions, and (d) weathering rates as determined by the ambient conditions. The COPR investigated in this study are exposed to a humid subtropical climate with monsoon rainfall occurring from July to September (~700 mm yr^{-1}). In contrast, previous studies have investigated COPR from sites located in the temperate climate zone with abundant rainfall throughout the year. Finally, (e) the age of the COPR is different, since the Indian COPR are relatively young (<25 yr) compared with COPR landfills investigated in other studies (between at least 40 and 180 yr). Additionally, the experimental design used in previous column studies using COPR did not allow the detection of possible nonequilibrium release mechanisms of Cr(VI). Nonequilibrium may prevail when the release of the contaminant depends on slow diffusion processes or when dissolution or desorption is kinetically controlled. Under these conditions, effluent conditions become sensitive towards pore water residence time. Assessing the release and transport of Cr from the COPR waste material, however, is essential for the evaluation of environmental risk and the adaptation of appropriate remediation strategies.

Therefore, the aims of the present study were (a) to investigate the release and transport of Cr from two young Indian COPR sites, and (b) to study the effects of flow interruptions on Cr release and leaching to assess possible nonequilibrium effects. Column experiments under water-saturated conditions were conducted to simulate Cr release from the wastes as caused by tropical heavy-rain events.

2 | MATERIALS AND METHODS

2.1 | Study site, sampling, and sample characterization

The COPR were sampled in 2011 after the monsoon season from two abandoned, illegally operated landfills in Rania (26°24′12.4′′ N, 80°02′51.2′′ E) and Chhiwali (26°11′45.8′′ N, 80°32′21.3′′ E). In Rania, surface COPR was taken with a spade from a 20-yr-old landfill, which was not covered by any material but left exposed to the atmosphere. In Chhiwali, COPR was obtained at the edge of a 10-yr-old heap, which had a thickness of ∼6 m and was covered by a 30-cm-thick quartz-rich sandy soil. The samples were manually homogenized, air dried, and sieved (<2 mm). Subsamples were ground in an agate ball mill (PM 400, Retsch). The substance density was determined by pycnometry. The main physical, chemical, and mineralogical properties of the COPR were described in Matern, Kletti, and Mansfeldt (2016).

2.2 | Column experiments

Duplicate column experiments were performed with the homogenized COPR fractions <2 mm. Supplemental Figure S1 shows a schematic of the experimental setup. The COPR material was packed into cylindrical columns made of polyvinyl chloride (PVC, EMC) with a length of 20 cm and an inner diameter of 4 cm. We are aware of the fact that the bulk density of the packed bed may differ from the field situation, since the COPR material had been homogenized and sieved. However, pretreatment was deemed necessary in view of a better reproducibility of the column packing. The inlet and outlet of the columns were capped with a polyethylene filter fleece (Terram 1000, Hüsker). For saturation, the columns were fed at the bottom inlet (upward flow) with a degassed solution at a flow rate $Q = 0.31$ cm^3 min^{-1} using a peristaltic pump (Ismatec MCP with a MS/CA 8-6 pump head, Ismatec Laboratoriumstechnik).

The solution had the composition of typical monsoon rain water according to Berner and Berner (1996): 0.47 mg Na$^+$ L^{-1}, 0.23 mg K$^+$ L^{-1}, 0.23 mg Mg^{2+} L^{-1}, 1.4 mg Ca^{2+} L^{-1}, 0.92 mg Cl$^-$ L^{-1}, 0.63 mg SO$_4^{2-}$ L^{-1}, and a pH of 6.0.

The duration and intensity of irrigation was derived from the natural monsoon precipitation in the study area. Two years of irrigation were simulated with a cumulative precipitation of 1,400 mm. Altogether, four irrigation phases were conducted, in each of which half of the annual precipitation (i.e., 350 mm) was applied within 24 h. Considering the cross-sectional area of the columns, this resulted in a flow rate of 18.33 mL h^{-1}. Between irrigation periods, flow interruptions of increasing duration served to investigate whether Cr release under irri-

gation was rate limited. Since flow interruptions increase the porewater residence time, we expected that effluent concentrations would increase if contaminant release was rate limited. The duration of each flow interruption differed by a factor of 10 (10, 100, and 1,000 h), which is sufficient for the detection of rate-limited processes (Wehrer & Totsche, 2003). The column effluents were sampled with two fraction collectors (SF-2120, Advantec, and Thomachron-0/219, Reichelt). Time-resolved sampling was performed in sampling intervals corresponding to 0.06–0.07 pore volumes (PV). To characterize the transport regime, a tracer pulse (0.01 M Cl$^-$) was injected after the irrigation cycles and the breakthrough curve was analyzed.

After the column experiments, the COPR material was removed in slices (∼5 cm thick) from the columns and finely ground. Chromate was extracted with carbonate hydroxide solution (0.28 M Na$_2$CO$_3$ in 0.5 M NaOH, pH 11.8–12.3) according to James, Petura, Vitale, and Mussoline (1995). For X-ray absorption spectroscopy (XAS) measurements, aliquots of the original COPR materials and the COPR from the columns were separately mixed with a pre-calculated amount of boron nitride and pressed into pellets. Spectra were collected in transmission mode at the Cr K-edge on beamline SAMBA at the SOLEIL synchrotron (Saint Aubin, France). The Si(220) double crystal monochromator was calibrated against the edge-energy (first maximum of first derivative) of a Cr metal foil set to 5,989 eV. The ion chamber detectors were filled with appropriate He/N$_2$ gas mixtures. The samples were cooled to ∼30 K using a He cryostat to prevent beam-induced oxidation or reduction of Cr. Data reduction was done using the software Athena (Ravel & Newville, 2005).

2.3 | Analysis of column effluents

The solution pH was measured potentiometrically using a glass electrode (Unitrode, Metrohm). The electrical conductivity was determined using a conductivity electrode (SevenEasy, Mettler-Toledo), and the ionic strength (I, mol L^{-1}) was estimated according to Griffin and Juinak (1973), where σ is the electric conductivity (in mS cm^{-1}):

$$I = 0.013\sigma \tag{1}$$

The abovementioned measurements were done directly after sampling to avoid CO$_2$ uptake from the atmosphere due to the high solution pH.

Chromium (VI) concentrations in the effluent were determined spectrophotometrically at 540 nm (Lambda 25 UV/Vis spectrometer, PerkinElmer) after reaction with diphenylcarbazide according to USEPA (1992). The concentrations of Ca, K, and Na were measured by flame atomic absorption spectrometry (AAS, iCE 3500, Thermo Scientific)

TABLE 1 Relevant solid phases for Cr(VI) leaching with their thermodynamic solubility constants [log (K_{sp})] reported in the literature and the range of calculated log(ion activity product [IAP]) and saturation index (SI) of the column leachates

Solid phase	Solubility reaction	log(K_{SP})	Range of calculated log(IAP)		SI	
			Rania	Chhiwali	Rania	Chhiwali
CAC-14	$Ca_4Al_2O_6(CrO_4)\cdot14H_2O_{(s)} +12H^+$ $\rightarrow 4Ca^{2+}+ 2Al^{3+}+ CrO_4{}^{2-} +$ $20H_2O$	71.02[a]	66.80 to 70.54	64.67 to 68.32	−4.22 to −0.48	−6.35 to −2.7
Calcium chromate	$CaCrO_{4(s)} \rightarrow Ca^{2+} + CrO_4{}^{2-}$	−2.27[b]	−5.48 to −4.55	−6.52 to −5.42	−7.75 to −6.82	−8.79 to −7.69
Cr(VI)-ettringite	$Ca_6Al_2(OH)_{12}(CrO_4)_3\cdot26H_2O_{(s)}$ $+12H^+ \rightarrow 6Ca^{2+} + 2Al^{3+}$ $+ 3CrO_4{}^{2-} + 38H_2O$	60.29[b]	55.84 to 61.22	52.77 to 56.56	−4.45 to 0.93	−7.52 to −3.73
Cr(VI)-katoite	$Ca_3Al_2(CrO_4)_{0.12}(O_4H_4)_{2.88(s)} +$ $11.52H^+ \rightarrow 3Ca^{2+} + 2Al^{3+} +$ $0.12CrO_4{}^{2-} + 11.52H_2O$	65.4[c]	−216.3 to −203.3	−222.7 to −211.0	−281.7 to −268.7	−288.1 to −276.4
Sodium chromate	$Na_2CrO_{4(s)} \rightarrow 2Na^+ + CrO_4{}^{2-}$	2.93[b]	−7.56 to −6.16	−7.81 to −5.71	−10.46 to −9.09	−10.74 to −8.64

[a]Perkins and Palmer (2001). [b]Visual Minteq 3.0 database. [c]Geelhoed et al. (2002).

with an air-acetylene flame and total Cr was quantified by AAS with a nitrous oxide-acetylene flame. Chromium(III) concentration was calculated as the difference between total Cr and Cr(VI). Aluminum, Fe, Mg and Si were analyzed by inductively coupled plasma optical emission spectrometry (ICP–OES, Ultima 2, Horiba Scientific). Aqueous concentrations of F^-, Cl^-, $NO_3{}^-$, and $SO_4{}^{2-}$ were determined by ion chromatography (ICS-1000, Dionex).

2.4 | Column data analysis

Bulk density (ρ_b) and PV were calculated from the dry weight of the packed bed divided by the void volume V_0 of the column and the saturated weight of the packed bed, respectively. The volumetric water content (θ) was obtained from bulk density and substance density (ρ_s) as $1 - \rho_b/\rho_s$. Mean porewater velocity (v_{eff}) was obtained from the flow rate (Q) [$v_{eff} = Q/(A \times \theta)$], where A is the cross-sectional area of the column. Normalized tracer concentrations (C/C_0) were obtained by the ratio of effluent and influent concentrations. Dimensionless time (number of PV eluted) was obtained by dividing the cumulative volume of effluent by the resident water volume.

The numerical code CXTFIT 2.1 (Toride, Leji, & van Genuchten, 1995) was used to determine the dispersion coefficient (D) and the retardation factor (R) by fitting the advection–dispersion equation to the Cl^- breakthrough data. Dispersivity (λ) is then given by D/v.

2.5 | Geochemical modeling

The geochemical equilibrium modeling program Visual Minteq 3.0 was used for the calculation of the solubility of solid phases, previously identified in COPR samples (Matern

et al., 2016). Therefore, activity coefficients were calculated with the Davies equation, which is valid for $I < 0.5$ mol L^{-1} (Pankow, 1991). The solid-phase thermodynamic database of Visual Minteq was complemented with thermodynamic data of the relevant solid phases cited from the literature (Table 1). In lack of a dedicated solubility product [log(K_{SP})] for CAC-14, the log(K_{SP}) for CAC-12 was chosen according to Perkins and Palmer (2001).

3 | RESULTS AND DISCUSSION

3.1 | Column experiment and modeling

Supplemental Table S2 summarizes the experimental conditions of the Cl^- breakthrough experiments and fitted parameters. Columns filled with Chhiwali COPR were more densely packed as compared with the columns with the Rania COPR, but in both cases the duplicates were very similar, resulting in similar ρ_b. Hence, the average values of θ and PV were slightly higher for the Rania columns. Supplemental Figure S2 shows the Cl^- breakthrough curves. Tracer breakthrough curves were symmetrical for both the Rania and the Chhiwali COPR indicating physical equilibrium and the absence of preferential flow. In nature, physical nonequilibrium due to heterogeneous flow conditions (preferential flow paths) is likely to control COPR leaching. This is due to a relatively broad aggregate size distribution (Geelhoed et al., 2003) caused by cementing and agglomeration (Dermatas, Bonaparte, Chrysochoou, & Moon, 2006). Hence, our experiments provide a worst-case approach by maximizing the contact area between the waste and the aqueous phase. Fits of the advection–dispersion equation to the Cl^- breakthrough curve were significant, with r^2 ranging from 0.99 to 1.00. The dispersion coefficient, D, ranged from 0.01 to 0.03 cm^2 min^{-1},
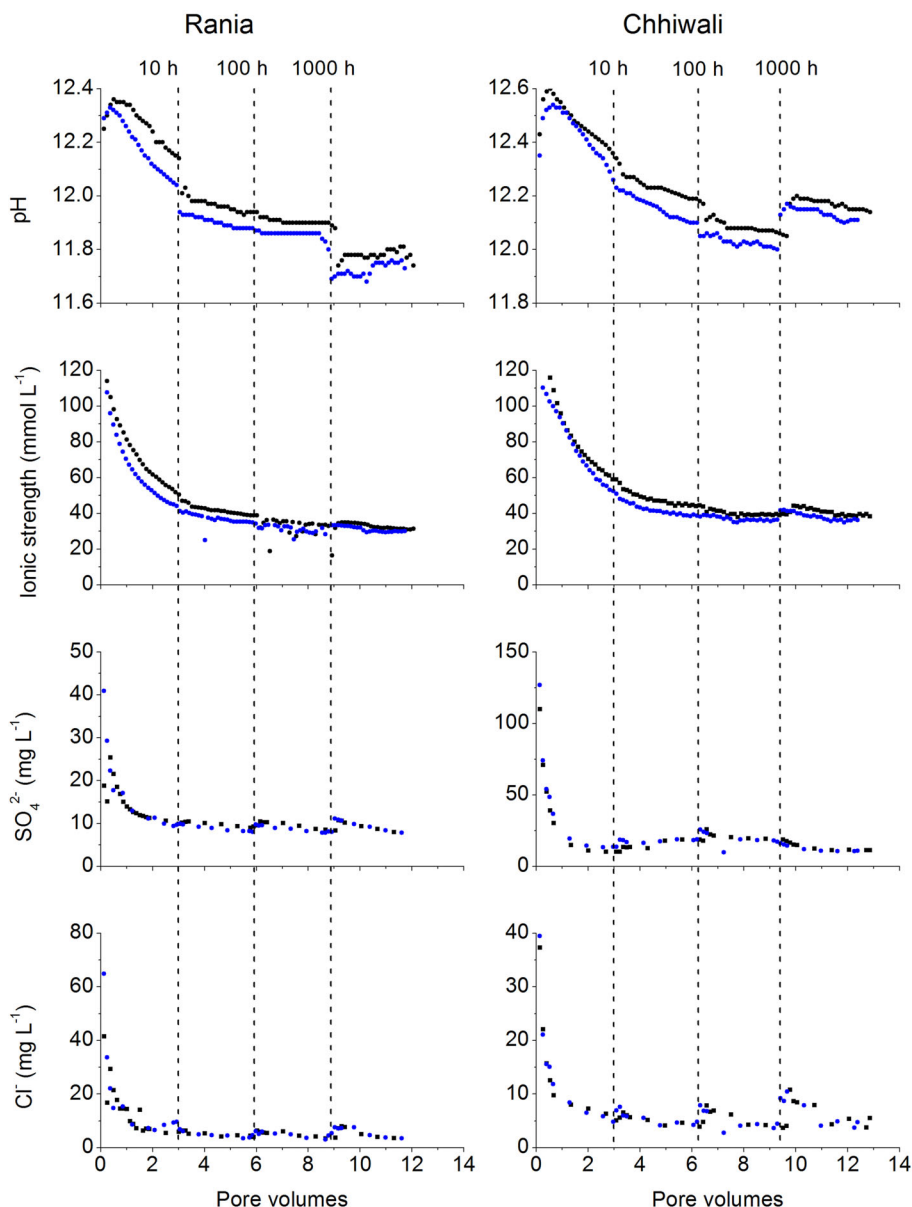
FIGURE 1 pH, ionic strength, and aqueous concentrations of Cl⁻ and SO₄²⁻ in the chromite ore processing residue (COPR) column effluents (black, Column A; blue, Column B). Dashed lines indicate flow interruptions with durations of 10, 100, and 1,000 h

resulting in λ values of 0.21 and 0.56 cm, respectively. The corresponding column Peclet number (Pe) values ranged from 36 to 95 indicating that the flow regime was advection dominated. Retardation factors, R, of 1.4 and 1.6 indicated that Cl⁻ was not a conservative tracer but slightly retarded during passage through the COPR material.

3.2 | Chromite ore processing residue leaching behavior

Figures 1 and 2 show the results of the COPR leaching as a function of the number of PV exchanged (dimensionless time). Aqueous concentrations of Al, Cr(III), Fe, Mg, and Si

are not shown, since their concentrations were very low (Fe, Mg, and Si were below the limit of determination by ICP–OES; 10 μg L⁻¹). During leaching, the pH decreased moderately from 12.3 to 11.7 (Rania COPR) and 12.6 to 12.1 (Chhiwali COPR). Considering that COPR has a high buffer capacity (Geelhoed et al., 2002), it is likely that alkaline pH values will prevail in the seepage water of COPR dumps in the next decades. The course of the ionic strength (as estimated from the EC, see Section 2) was similar for both COPR. Starting from values of ~120 mmol L⁻¹, the ionic strength decreased exponentially and leveled off at values of 30 mmol L⁻¹ (Rania COPR) and 40 mmol L⁻¹ (Chhiwali COPR) after leaching of 6 PV. This may suggest the coexistence of two pools of COPR constituents, where a highly
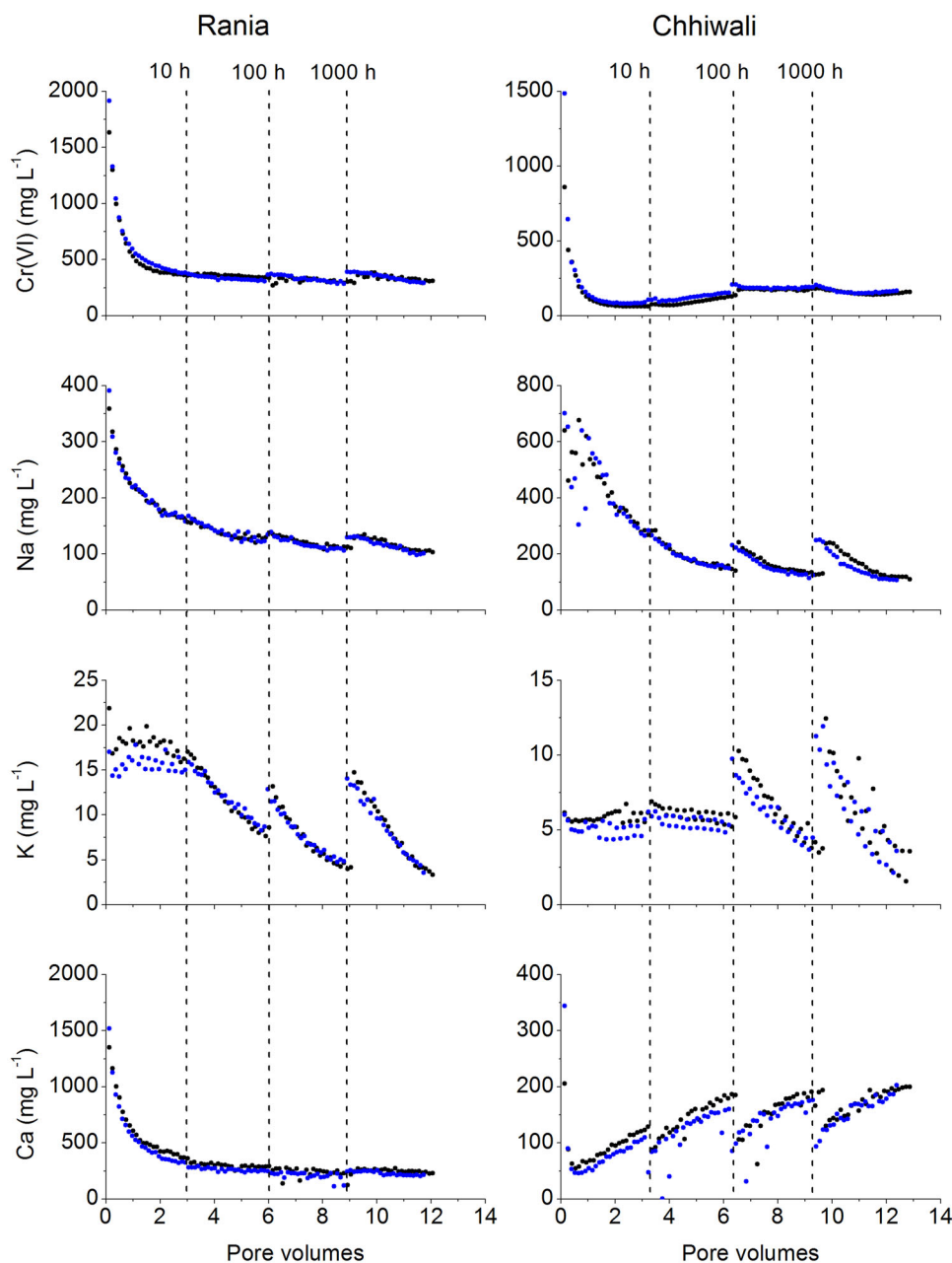
FIGURE 2 Aqueous concentration of Cr(VI), Na, K, and Ca in column experiments with chromite ore processing residue (COPR) (black, Column A; blue, Column B). Dashed lines indicate flow interruptions with durations of 10, 100, and 1,000 h

mobile pool of COPR constituents was leached out rather quickly (6 PV correspond to 1 yr of precipitation), whereas comparably high base-level concentrations were provided by a further pool.

The course of the individual analytes shows that the ionic strength was dominated by Ca^{2+}, CrO_4^{2-}, and Na^+, whereas SO_4^{2-}, Cl^-, and K^+ contributed marginally. Leaching characteristics of the individual components differed [i.e., steady-state levels of Cr(VI) and Ca were attained after exchange of 3 PV, whereas Na approximated base level concentrations after 6 PV in both COPR].

Hexavalent chromium was truly a major solution phase component in the COPR leachates. This holds for both the leaching maxima and the base levels. The Cr(VI) concentration in the leachate decreased from 1,800 to 300 mg L^{-1} in the Rania COPR and from 1,200 to 163 mg L^{-1} in the Chhiwali COP during 12 PV (2 yr of monsoon precipitation). These Cr(VI) concentrations are four to five orders of magnitude above the World Health Organization drinking water standard of 0.05 mg L^{-1} (WHO, 2011). Compared with Geelhoed et al. (2003), who leached COPR material from Glasgow, the Cr(VI) concentrations in leachates were around 50-fold higher

in our study. Integration of the leaching curves indicated that 37% (Rania COPR) and 17% (Chhiwali COPR) of the leached Cr(VI) mass was released during the first 3 PV. Considering the total Cr(VI) contents of the investigated COPR (16.5 g kg^{-1} Rania COPR and 9.2 g kg^{-1} Chhiwali COPR), the Rania COPR has a lot more exchangeable Cr(VI) than the Chhiwali COPR. The high Cr(VI) concentrations at the beginning of leaching may be attributed to a highly mobile contaminant pool that was transferred into porewater during column saturation and then displaced by the uncontaminated influent. Conversely, the plateau values of Cr(VI) approximated after ∼3 PV may have resulted from the steady-state release driven by the amount of Cr(VI) mobilizable under the specific flow conditions. Alternatively, the initial and base level concentrations may also be attributed to the dissolution of distinct host phases differing in solubility. With respect to the age of the investigated COPR, it is likely that the leaching of young COPR leads to higher leaching maxima and base level concentrations compared with older COPR, in which Cr(VI) is primarily bound in calcium aluminate mineral phases.

To investigate whether release kinetics controlled COPR leaching, three consecutive flow interruptions of increasing duration (10, 100, and 1,000 h) were performed (Figures 1 and 2). Our results show that Cr(VI) concentrations responded only very moderately to the flow interruptions. Thus, base level concentrations can predominantly be attributed to equilibrium between solid and solution phases. This was not the case for Na (Chhiwali COPR) and K (both COPRs). Here, the second and third flow interruptions caused a prominent increase of effluent concentrations pointing to rate-limited release. The opposite was the case for Ca in the Chhiwali COPR where flow interruptions led to an initial decrease of the effluent concentrations with resumed percolation and concentrations rebounded with prolonged irrigation. Thus, increased residence times favored Ca retention. The contrasting response to flow interruptions observed for Na and K, on the one hand, and for Ca, on the other, may point to diffusion-limited cation exchange processes between Na$^+$, K$^+$, and Ca^{2+}. Regarding the charge balance in the solution it is likely that Ca^{2+} ions were retained in charge-equivalent amounts to the Na$^+$ ions released.

3.3 | Possible solubility-controlling phases in chromite ore processing residue

Supplemental Table S3, as well as Supplemental Figures S3a and S3b, show the solid phases identified in both COPR by X-ray powder diffraction (XRD) in a previous study. The high pH of the leachate was primarily caused by the dissolution of alkaline earth metal hydroxides present in COPR. Portlandite is formed rapidly upon hydration of excess quicklime (additive used in the high-temperature roasting process) during the

early stages of transport and landfilling (Chrysochoou et al., 2010). The high-effluent pH in the early stages of the column experiments is in line with the dissolution of portlandite (pH ∼ 12.4), which was also observed in a drainage ditch of COPR in the northwest of England (Deakin et al., 2001a). However, leaching studies performed with hydrocalumite and hydrogarnet show that these phases have an equilibrium pH in the range of 11–12 (Atkins, Macphee, Kindness, & Glasser, 1991), indicating the importance of other minerals for the pH and buffering of COPR.

Sjogrenite, Cr(VI)-ettringite, calcium aluminum chromium oxide hydrate (CAC), katoite, and chromates of the alkaline and alkaline earth metals are potential host phases identified by XRD or scanning electron microscopy (SEM) that may control the Cr(VI) concentration in the leachates.

Sjogrenite is structurally related to CAC and is able to substitute Cr in the mineral structure or to retain CrO$_4$$^{2-}$ in the interlayer. Wazne et al. (2008) reported that hydrotalcite may control the solubility of Cr(VI) through anion exchange. Since hydrotalcite is stable in the range of pH prevalent in our study (Chrysochoou et al., 2009), it is a viable candidate for solubility controlling phase for Cr(VI) at least in the Rania COPR, where it was present in low contents.

Ettringite is a hydration product of brownmillerite that may substitute CrO$_4$$^{2-}$ for SO$_4$$^{2-}$. It was only detected in the Rania COPR via SEM (Matern et al., 2016). Energy-dispersive X-ray (EDX) analyses indicated CrO$_4$$^{2-}$ substitution in ettringite crystals. The saturation index (SI) of Cr(VI)-ettringite varied from −4.45 to 0.93 for the Rania COPR leachate and −7.52 to −3.73 for the Chhiwali COPR leachate (Table 1), which is in the range of values reported by Geelhoed et al. (2002). Based on COPR leaching tests, Chrysochoou and Dermatas (2006) concluded that Cr(VI)-ettringite was only stable in a narrow pH range of 10.9–11.2. In view of the pH course observed in our column experiments, Cr(VI)-ettringite was presumably not stable, resulting in its dissolution. Considering the low content of Cr(VI)-ettringite in the COPR, the release of Cr(VI) caused by dissolution of Cr(VI)-ettringite was thus negligible.

CAC-14 is isostructural to hydrocalumite and is a layered double hydroxide mineral known to have a high anion exchange capacity with CrO$_4$$^{2-}$ anions held in the interlayers (Palmer, 2000; Wazne et al., 2008). Katoite, often referred to as hydrogarnet, is a hydration product of brownmillerite and able to substitute Cr(VI) in its tetrahedral structure (Hillier et al., 2003; Hillier, Lumsdon, Brydson, & Paterson, 2007). Both CAC-14 and katoite are major minerals identified in the investigated COPR. The observed SI of CAC-14 in the Rania COPR leachate varied from −4.22 to −0.48, and for the Chhiwali COPR leachate varied from −6.35 to −2.70. Except for one sample at the beginning of leaching, the SI are altogether lower than zero (Table 1), indicating that the leachate

was undersaturated with respect to CAC-14. This holds for Cr(VI)-katoite with SI of −281.7 and −268.7 (Rania) and between −288.1 and −276.4 (Chhiwali) (Table 1). Bearing in mind that the leachates were undersaturated with respect to all calcium aluminate phases, it is remarkable that the flow interruptions indicated chemical equilibrium. Modeling results of Geelhoed et al. (2002) indicated that Cr(VI) concentrations in the leachates can be accurately described assuming mineral equilibrium with Cr(VI)-ettringite, Cr(VI)-hydrocalumite, and Cr(VI)-hydrogarnet for the pH range between 10 and 12, which was the case in our experiment. Geelhoed et al. (2002) used the calculated ion activity products (IAPs) from batch experiments as an estimate of mineral solubility. Applying their $\log(K_{SP})$ to the COPR leaching observed in our experiments suggests chemical equilibrium with respect to CAC-14. This is in line with results by Wazne et al. (2008), who concluded from leaching experiments that the COPR continuously leaches Cr(VI) at concentrations equivalent to the solubility of Cr(VI)-hydrocalumite. This was also the case in the experiments of Chrysochoou and Dermatas (2006), who reported that Cr(VI) bound in hydrocalumite was constant in the pH range of 11.3 and 12.4 and led to Cr(VI) leachate concentrations of below 50 mg L^{-1}. Geelhoed et al. (2002) reported a Cr(VI) concentration of 20 mg L^{-1} at the equilibrium pH of COPR. It can therefore be assumed that the CAC were also a source of Cr(VI) in our study.

Due to the stability of Ca-Al phases (Table 1) down to pH 11 (Chrysochoou et al., 2009), the initial high Cr(VI) concentration in the leachates cannot be explained by the solubility control of the abovementioned mineral phases. In the Chhiwali COPR, easily soluble compounds such as Na_2CrO_4 and Na_2SO_4 were detected by SEM (Matern et al., 2016). They were present in aggregates and thus possibly protected from in situ leaching but became accessible by the exposure of inner surfaces during sieving. It is likely that these easily soluble phases are also present in the Rania COPR due to the similar production processes, age of landfill, and weathering conditions. For the Rania COPR, leaching characteristics of Cr(VI) and Na were quite similar, whereas they differed for the Chhiwali COPR. Leachates of both samples were distinctly undersaturated with respect to Na_2CrO_4, with SI ranging from −10.46 to −9.09 for the Rania COPR and −10.74 to −8.64 for the Chhiwali COPR. The molar Na/CrO_4^{2-} ratio in the Chhiwali leachates was about 2:1 at the end of the last two irrigation phases (Supplemental Figure S4), indicating that Na_2CrO_4 contributed partially to Cr(VI) release. However, the molar Na/CrO_4^{2-} ratio in the Rania leachate was nearly constant and close to 1:1 (Supplemental Figure S4), so that further unknown sources may be relevant in this case (e.g., $CaCrO_4$). To the best of our knowledge, dissolution of highly soluble Cr host phases combined with their detection in the solid phase has not been reported before. It is likely that the COPR investigated in other studies no longer contained such

highly soluble Cr sources due to greater age and weathering. In a previous study of Breeze (1973), it was shown that Na and Cr leached in quantities, which could account for Na_2CrO_4. However, the sample was extracted with dilute acid, which may significantly influence leaching behavior. Furthermore, Breeze (1973) pointed out that the CrO_4^{2-} in the waste was rather a mixed salt of more than one cation. James (1994) suggested that moderately soluble phases such as $CaCrO_4$ may be responsible for Cr(VI) leaching from COPR located in areas of Hudson County, New Jersey. The author detected crusts, which contained CrO_4^{2-} salts on the surface of poorly drained soils, from which evaporation took place. The SI with respect to $CaCrO_4$ ranged from −7.75 to −6.82 in the Rania leachate and from −8.79 to −7.69 in the Chhiwali leachate, which is in the range of log(IAP) reported in other studies (−4.8, Deakin et al., 2001b; −8.77, Geelhoed et al., 2002). Although $CaCrO_4$ was not detected in the COPR used in our study, its role as a possible solubility-controlling phase cannot be excluded.

3.4 | Extractable chromate and chromium oxidation state in the chromite ore processing residue solid phase

Table 2 summarizes the extractable amounts of CrO_4^{2-} and the ratio of $Cr(VI)/Cr_{total}$ in the COPR as determined by X-ray absorption near edge structure (XANES) spectroscopy (Supplemental Figures S5 and S6). In the lower column section (inflow side), the ratio $Cr(VI)/Cr_{total}$ decreased. Since no Cr(III) was leached, this reflects the depletion of solid-phase Cr(VI) by leaching. The XANES results correspond to a cumulative Cr(VI) export of 2.7 g kg^{-1} for the Rania COPR and 1.5 g kg^{-1} for the Chhiwali COPR, equivalent to 16% of the initial Cr(VI). The depth dependency of the Cr(VI) was confirmed by the Cr(VI) extractions of the solid phase after the column experiments. For both COPR samples, most of the Cr(VI) initially present was leached out from the lower section (inflow side) of the columns.

The extraction data indicate that, altogether, the Cr(VI) content in the lower column section was reduced by ∼38% in the Rania COPR and by 40% in the Chhiwali COPR. In the upper column section, no Cr(VI) was leached out from the Rania COPR, and a marginal amount of 3% was leached from the Chhiwali COPR. These findings are consistent with the base levels of Cr(VI) found in the leaching experiments. Since the reservoir of Cr(VI)-bearing mineral phases was obviously not depleted within the course of 12 PV (i.e., the total duration of the experiments), effluent concentrations remained fairly constant. With respect to the leaching behavior of Cr(VI) and the presence of extractable CrO_4^{2-} in the solid phase, it seems likely that a small amount of Na_2CrO_4 present in the COPR was rapidly dissolved at the beginning of leaching, leading to the high initial Cr(VI) concentrations. Once the Na_2CrO_4

TABLE 2 Cr(VI) concentration extracted with a carbonate hydroxide solution (0.28 M Na_2CO_3 in 0.5 M NaOH) according to James et al. (1995) and solid-phase Cr(VI)/Cr_{total} fractions in column sections at the end of the column leaching experiments as estimated from the pre-peak intensity of Cr K-edge XANES spectra (Supplemental Figure S5)

	Rania		Chhiwali	
Depth[a]	**Cr(VI) concentration**	**Cr(VI)/Cr_{total}**	**Cr(VI) concentration**	**Cr(VI)/Cr_{total}**
cm	g kg^{-1}		g kg^{-1}	
0–3	16.4	0.39	8.9	0.19
3–10	14.7	0.38	8.4	0.22
10–17	13.4	0.35	7.5	0.17
17–20	10.2	0.31	5.5	0.17
$\bar{x}$[b]	13.8		7.7	

[a]The flow direction was from 20 cm (inlet) to 0 cm (outlet). [b]Cr(VI) contents before the column experiment were 16.5 g kg^{-1} (Rania) and 9.2 g kg^{-1} (Chhiwali).

pool was depleted, the leachate concentrations dropped and may have been controlled by CAC, leading to a solution that was undersaturated with respect to Na_2CrO_4. Assuming mineral equilibrium with respect to CAC after a certain transport distance into the column, dissolution of CAC only occurred near the column inflow section. Thus, the amount of Cr(VI) was depleted in the lower section and almost constant in the upper outflow section.

4 | CONCLUSIONS

Our experimental results clearly showed that Cr(VI) in both COPR wastes is highly soluble and consequently forms a major solution component in the leachates, with concentrations exceeding the current World Health Organization drinking water standard (0.05 mg L^{-1}) by four to five orders of magnitude. The extremely high initial concentrations of Cr(VI) in the leachates, followed by high base levels over the entire leaching period, may arise from rapid initial dissolution and leaching of Na_2CrO_4 and chemical equilibrium with CAC-14 solid phases, respectively. The chemistry of the Indian COPR differed from that studied in previous reports, which was explained by its young age and the specific monsoonal weathering conditions. Overall, from our results, we expect that Cr(VI) will continue to be leached from the COPR dumpsites near Kanpur. Since the COPR materials are characterized by a highly alkaline pH and high pH-buffering capacity, long-term inputs of alkaline, Cr(VI)-rich leachates into underlying aquifers must be expected, with Cr(VI) concentrations of up to 100–300 mg L^{-1} (the observed base levels of the leaching curves). Taking the field conditions and thickness of the COPR dumps into account, Cr(VI) leaching must be expected to continue for centuries with obvious consequences for downstream groundwater quality. Thus, aside from well water treatment and groundwater remediation, a removal or stabilization of the COPR dumpsites is mandatory.

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