



Chemical and mineralogical characterization of chromite ore processing residue from two recent Indian disposal sites



Katrin Matern ^a, Holger Kletti ^b, Tim Mansfeldt ^{a,*}

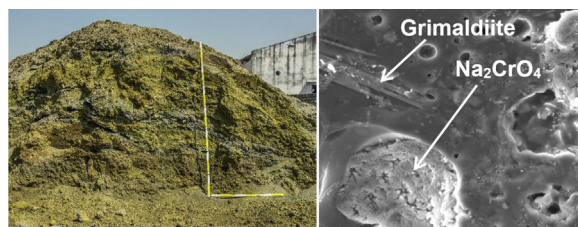
^a Soil Geography/Soil Science, Department of Geosciences, University of Cologne, Albertus-Magnus-Platz, 50923 Cologne, Germany

^b FA. Finger-Institut für Baustoffkunde, Bauhaus-Universität Weimar, Coudraystraße 11, 99421 Weimar, Germany

HIGHLIGHTS

- Relatively young (<25 years) COPR waste was investigated.
- A new Cr host mineral, grimaldiite [CrO(OH)], could be identified.
- Well soluble Na₂CrO₄ was present in the waste.
- A modified total microwave digestion method was examined.

GRAPHICAL ABSTRACT



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ABSTRACT

Chromite ore processing residue (COPR) is a hazardous waste. Nevertheless, deposition of COPR in uncontrolled surface landfills is still common practice in some countries. Whereas old (between at least 40 and 180 years) COPR from the temperate zone has been intensively investigated, information on COPR in other regions is restricted. Relatively young (<25 years) COPR samples obtained from two abandoned landfill sites in India were investigated by a modified total microwave digestion method, X-ray powder diffraction (XRPD), and scanning electron microscopy (SEM) in order to determine their chemical and mineralogical nature. By the use of microwave digestion with acid mixtures of HNO₃, H₃PO₄, and HBF₄ (5:3:2 vol), COPR was completely dissolved and element contents similar to those obtained by X-ray fluorescence were found. Total Cr contents of the two COPR accounted for 81 and 74 g kg⁻¹, of which 20 and 13% were present in the carcinogenic hexavalent form (CrVI). Apart from the common major mineral phases present in COPR reported earlier, a further Cr host mineral, grimaldiite [CrO(OH)], could be identified by XRPD and SEM. Additionally, well soluble Na₂CrO₄ was present. Improving the effectiveness of chromite ore processing and preventing the migration of Cr(VI) into water bodies are the main challenges when dealing with these COPR.

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1. Introduction

Chromite ore processing residue (COPR) is a waste of the chromate (CrO₄²⁻) extraction roasting process and is still deposited in the environment in large amounts in some newly industrialized

countries. In the past, the waste has been produced in several industrial areas, such as Glasgow, Scotland (Farmer et al., 1999) and Hudson County, New Jersey, USA (Burke et al., 1991; Weng et al., 1994) and this process is still being used in, for example, China, Russia, Kazakhstan, Pakistan, and India (Darrie, 2001). Darrie (2001) estimated that high-lime process plants generated about 600,000 Mg of COPR in 2001.

Chromite ore processing residue is strongly alkaline, with pH

* Corresponding author.

E-mail address: tim.mansfeldt@uni-koeln.de (T. Mansfeldt).

values varying from 11 to 12.5 (Chrysochoou et al., 2009a; Deakin et al., 2001; Foeldi et al., 2013). Residual Cr contents of waste COPR range from 20 to 110 g kg⁻¹ (Farmer et al., 1999; Foeldi et al., 2013; Geelhoed et al., 2003), of which up to 30% is present as hexavalent Cr (Cr(VI)) (Geelhoed et al., 2003). After deposition, COPR is not stable and undergoes weathering reactions, which results in destabilization and dissolution of Cr(VI)-bearing minerals (Chrysochoou et al., 2010; Geelhoed et al., 2001, 2002). Hence contamination of groundwater is a key environmental risk arising at COPR sites.

In a previous work (Foeldi et al., 2013), we investigated 21 samples from uncontrolled operating disposal sites and surrounding soils in the area of Kanpur, Uttar Pradesh, North India. These sites were affected by the production of Cr tanning agents. Considering that six samples were clearly identified as highly Cr-contaminated COPR (Foeldi et al., 2013), a detailed study of the mineralogy and chemistry of the source COPR is needed.

This study focuses on two production sites of Cr(III) salts used in leather tanning near Kanpur. The first site reported in this paper is Rania, to the west of Kanpur in the district of Kanpur Dehat, where Cr works were in operation from the late 1980s until 2005. One heap covers an area of ~1 km² and contains ~30,000 Mg of waste (Jaiswal and Braun, 2010). At the second site, in Chhiwali, to the southeast of Kanpur in the district of Fatehpur, two Cr works were established in 2004 and are still operating. Chromite ore processing residue is found in large landfill sites as well as elsewhere in these areas, because it is commonly used in road construction, berms, and foundation material and for backfill, due to its sand-like properties.

Although the mineralogy and solid-state speciation of Cr in COPR deposits have been widely studied in the USA (Boecher et al., 2012; Chrysochoou and Dermatas, 2007; Chrysochoou et al., 2009a, 2010; Dermatas et al., 2006) and Europe (Farmer et al., 1999; Geelhoed et al., 2002; Hillier et al., 2003; Thomas et al., 2001), the present findings cannot be simply transferred to the Indian sites: COPR from various localities may differ in their chemical and mineralogical compositions due to differences in (i) chromite ore composition, (ii) extraction process, (iii) deposition technique, and (iv) ambient weathering conditions. Previous studies have investigated COPR from sites located in the temperate zone. The Indian sites, however, are in the humid subtropical climate zone with a dry winter season and a three-month monsoon period. Finally, (v) the factor of time is different because the Indian COPR are relatively young (<25 years) compared to the Glasgow and North American COPR (between at least 40 and 180 years).

Thus, the aim of the present study was to investigate the chemical and mineralogical characteristics of COPR obtained from two abandoned landfill sites in India. We expected that the Cr content of these COPR would be higher compared to the Glasgow and North American COPR, because of the limited leaching time during the monsoon period as well as the short time of landfilling. We also assumed that the mineral phases would differ, which might be important regarding the leaching behavior of these COPR. Scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD) complemented by other laboratory analyses were performed to investigate these objectives. Furthermore, a modified total microwave digestion method was examined, since it is important to evaluate different methods to accurately determine the total Cr contents of the waste. The results presented in this study provide an improved understanding of these COPR wastes and are essential for the evaluation of environmental risks and remediation strategies.

2. Material and methods

2.1. Sites, sampling, and sample preparation

The COPR was sampled from two abandoned, illegally operating disposal sites in Rania and Chhiwali in the State of Uttar Pradesh. In Rania, surface COPR was taken with a spade from a 20-year-old landfill, which was not covered by any material but left exposed to the surface. In Chhiwali, COPR was obtained at the edge of a 10-year-old landfill which had a thickness of about 6 m and was covered by a 30-cm-thick layer of quartz sand. Sampling took place during the dry season in order to obtain dry material. The samples were manually homogenized by intensive stirring for 10–15 min with a big shovel, air dried, and sieved (<2 mm). Particles >2 mm were separated for backscattered electron (BSE) images and secondary electron (SE) images. Subsamples were ground in an agate ball mill (PM 400, Retsch).

2.2. Analyses of chemical composition

Particle size distribution was analyzed with a laser particle analyzer (Beckman Coulter LS13 320). Prior to the analyses, carbonates were destroyed with HCl. The COPR pH was measured potentiometrically using a glass electrode (Unitrode, Metrohm) both in 0.01 M CaCl₂ solution and in deionized water with a solid:solution ratio of 1:5. Total C, N, and S were quantified with a CNS analyzer (Vario EL, Elementar). Organic C was determined with the same equipment by adding 10% HCl to the weighed samples. Inorganic C was calculated as the difference between total and organic C. The chemical composition was analyzed by wavelength dispersive X-ray fluorescence (XRF; Axios, PANalytical, further details are provided in supplementary materials (SM)).

Due to the importance of accurate determination of the total Cr content of the waste, two different total digestion methods were evaluated. Since it is used by researchers in many countries for the determination of metals, a pseudo-total aqua regia digestion method was also performed. Detailed information on the digestion methods are listed in the SM.

Chromate in the wastes was selectively extracted with (1) deionized water (pH 5.7) for soluble CrO₄²⁻, (2) phosphate buffer (5.0 mM K₂HPO₄ in 5.0 mM KH₂PO₄, pH 7.0) for exchangeable CrO₄²⁻, and (3) carbonate-hydroxide solution (0.28 M Na₂CO₃ in 0.5 M NaOH, pH 11.8 to 12.3) for insoluble CrO₄²⁻ according to James et al. (1995) (further details are provided in the SM). Since in a previous study by Farmer et al. (2006) it was found that milling the COPR prior to base digestion almost doubles the release of Cr(VI), additionally milled samples were used in step 3. Chromium(VI) concentration in the eluates was determined spectrophotometrically at 550 nm (Lambda 25 UV/Vis Spectrometer, PerkinElmer) with diphenylcarbazide (US EPA, 1992) immediately after filtration.

2.3. Analyses of mineralogical composition

The X-ray diffraction measurements were recorded on a Bruker D8 Advance diffractometer in Bragg-Brentano geometry. The wavelength used was Cu K α radiation generated at 40 kV and 40 mA and selected via a Bruker SolX energy dispersive detector. The measurement range was 4° 2 θ to 70° 2 θ with a step size of 0.02° and a counting time of 4 s per step. Each sample was measured twice. Sample preparation and phase identification are described in the SM.

For SEM, all samples were examined in an FEI Nova NanoSEM 230, an ultra-high resolution SEM with low vacuum, using a beam accelerating voltage of 12 kV. Quantitative and qualitative elemental analyses were performed with an energy-dispersive X-

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