Research Article

Mineral processing: leaching process of chromium and recovery of platinum group elements from Northwestern Saudi Arabian Ophiolitic chromite

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Abstract

The current strategy reports the recovery of precious group metals (PGMs) from Na_2CO_3 roast of Saudi Arabian ophiolitic chromite ore at 1160 °C under atmospheric O_2. The influence of roasting temperature (960–1200 °C) and leaching agents (H_2O, HCl, H_2SO_4) and their concentrations on the recovery of PGMs was studied. Chromite roast concentrates a reasonable percentage of approximately 45% with an overall 43% Cr_2O_3. PGMs in the original ore was petitioned and ends up in Na_2CrO_4 liquor whereas the liquor and a solid roast residues contained the rest of chromite components (Fe_2O_3, Al_2O_3, others). Na_2CrO_4 in the water or H_2SO_4 leachate was reduced with SO_2 gas to give crystalline basic chrome sulfate with excellent yield (> 99%) and purity (Fe < 0.1%). PGMs in the Na_2CrO_4 liquor were extracted into methylisobutylketone (MIBK) after shaking with ammonium pyrrolidine dithiocarbamate (APDC). In MIBK extract, the PGMs species was then stripped by shaking with $HgCl_2$–HNO_3 (1.0 mol L^{-1}). Ir and Pt in the produced PGEs cake were found up to 4.0 and 0.5 μg/g, respectively whereas the majority of Ni (0.5% as NiO) was retained in the solid roast residues. The proposed method offers a simple approach with good cost-effectiveness for PGEs recovery and production of basic chrome sulfate with Fe content less than 0.1%. Leaching with water offers a simple, an eco-friendly and cost-effectiveness approach for the production of a basic chromium sulfate product with high quality yield of PGEs as a byproduct with minimum Fe content (< 0.1% m/m) required for the tanning industry compared to the method reported.

Keywords Saudi Arabian chromite ore · Chromite–Na_2CO_3 roast · Platinum group elements · Basic chromium sulfate · Leaching · Liquid–liquid extraction

1 Introduction

It is well known, chromite mineral is a solid solution of four different spinels form a combination of the following potential end members: $FeAl_2O_4$, $MgAl_2O_4$, $FeCr_2O_4$, $MgCr_2O_4$, Fe_3O_4 and $MgFe_2O_4$ spinels [1]. The ophiolitic chromites defined as $\{(Fe,Mg)(Cr,Al,Fe)_2O_4\}$ are characterized by different contents and assemblages of PGM's.

Variable PGE contents (0.033–1.88 μg/g) and enrichment in Os, Ir and Ru have been reported from chromite deposits from Mayari-Baracoa ophiolite belt in Eastern Cuba [2]. Ophiolitic chromites from south west of Turkey are enriched in IPGM (Os, Ir, and Ru) over PPGM (Pt, Pd, and Rh) with PGM concentrations between 61 and 1305 μg/kg [3, 4]. Berit chromites in SE Turkey contain Pt (10–1155 μg/kg) and Pd (3–2518 μg/kg) enrichments [5]. The chromites

from Middle Arm. Brook (Newfoundland, Canada) are characterized by relatively high total PGEs (up to 1028 µg/g) with enrichment in PPGE relative to IPGE [5]. The Pindos ophiolite complex, north-western Greece hosts various chromites deposits and are characterized by low PGE grades with a few localities in the area of Korydalos (SE Greece) enriched in PGMs +Au (up to 29.3 µg/g) [6].

Bearing the fact that the environment liability on manufacturing is increasing, research must focus on the development of other processing directions, which lighten the delicate of wastes, materials and energy, by dropping the time for handling and falling the waste volume at the end of the process [7]. Saudi Arabia Ophiolitic chromites from Al' Ays area contain PGM's with maximum values of 2.570, 0.687, 0.840, 5.800, 6.200, and 3.300 µg/g for Pt, Pd, Rh, Ru, Ir and Os, respectively with an average of total PGM's (40 samples) about 972 µg/kg and about 1500 µg/g Ni [8, 9]. The continued interest in ophiolitic chromites arises from the fact that the single largest resource of PGMs in the world is the layers of chromite in the Bushveld complex South Africa. The ophiolitic chromitites have been extensively investigated worldwide for the possible occurrence of PGM's [10]. The enrichment and extraction of PGEs from Bushveld type chromite ore has been reported by magnetic, gravity and flotation technologies (physical separation) [10–15].

Leather tanning industry and the use of PGEs are the important and growing industries in Saudi Arabia (SA) and annually consumes about 3000 tons (imported) of basic chrome sulfate (Tanning and leather goods committee, Jeddah, Chamber of Commerce and Industry, Personal communication). Low grade and low tonnage of Saudi chromite ore and the fine grain size of the platinum group minerals (less than 20 microns) make them not amenable for flotation.

PGMs are vital for the progress of recent manufacturing as well as designing and developing high technology products in our daily lives. Hence, the worldwide demand of PGEs is rising quickly and predicted to surpass the supply by 40,000 tons annually. PGEs (Pt, Pd, Ir, Os, Rh, Ru) are often linked with gold and are of main profitable significance [16–19]. Recently, magnetic solid phase extraction has been used for the separation of PGMs from leach solutions and wastewater [20]. PGMs have very few occurrences where they are present in an ore deposit at economically extractable levels [21, 22]. PGMs are energetic elements for the developing of existing production as well as planning and developing high technology products used in our daily lives. Moreover, as far as the authors are aware, the enrichment and recovery of PGMs from Saudi Arabian chromite ore is of great interest and importance and it has not been attempted. Therefore, a lab scale attempts to use Saudi ophiolitic

chromite for recovery PGMs and production and basic chrome sulphate is of great importance in recent years. Hence, the present study is focused on: (1) Enrichment of PGMs and Ni through separation of Cr_2O_3 which constitutes about 50% of chromite; (2) Recovery of PGM's (byproduct) by solvent extraction using methylisobutylketone (MIBK) and the complexing agent ammonium pyrrolidine dithiocarbamate (APDC); and finally (3) Developing of efficient procedures for the production of basic chromium sulfate [$(Cr_2(SO_4)_2 (OH)_2)$] (Target component for leather tanning industry) from chromite ore processing residue using low cost, efficient and eco-friendly leaching agent such as water and/or H_2SO_4.

2 Materials and methods

2.1 Reagents and materials

All chemicals and solvents used were of analytical reagent grade. Low density polyethylene (LDPE) bottles, Nalgene were carefully cleaned first with hot detergent, soaked in 50% HCl (Analar), HNO_3 (2.0 mol L^{-1}), subsequently washed with dilute HNO_3 (0.5 mol L^{-1}) and finally rinsed with distilled water. LDPE bottles were used for leaching experiments of the chromite ore–Na_2CO_3 roast with the leaching agents (H_2O, HCl, H_2SO_4). A stock solution (0.1% w/v) of the reagent ammonium pyrolidine dithiocarbamate (Merck, Darmstadt, Germany) was prepared in acetone. A series of standard BDH solutions (Poole, England) solutions (100 µg mL^{-1}) of the PGM's and nickel were prepared in dilute nitric acid. Saudi Arabian Ophiolitic chromite ore samples were collected from Wadi Al Hawanet and Jabal Al Wasq areas.

2.2 Apparatus

A Perkin Elmer inductively coupled plasma-optical emission spectrometry (Optima 4100 DC Shelton, CT, USA) was operated at the optimum operational parameters for determination of the major elements. A Perkin Elmer ICP-MS Sciex model Elan DRC II (California, CT, USA) was used for analysis of PGMs at the optimized operational parameters. Deionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA). Digital micropipettes 10–1000 µL (Volac) were used for preparation of more diluted solutions. A pH Meter (Thermo Orion model 720, Fisher Scientific, MA, USA) was employed for pH measurements.

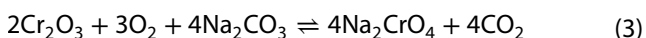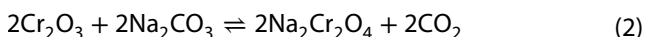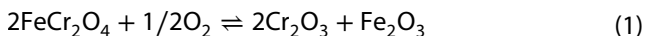## 2.3 Experiment #1: determination of chemical composition of chromite ore

Different methods have been used for the dissolution of chromite, e.g. lithium tetraborate flux [23], sodium peroxide fusion and mixtures of HNO_3, HF and $HClO_4$ [21], MnO_2–$LiSO_4$–sulphuric acid mixtures [24]. In this study, four Saudi Arabian chromite ore samples collected from Wadi Al Hawanet (samples I–III) and Jabal Al Wasq (sample IV) areas were digested in the acid mixture of $HClO_4$–HNO_3–HF (1:1:1 v/v) for 3 h [25]. The resultant solutions were analyzed for major and, trace elements, and PGM's by ICP-OES and/or ICP-MS.
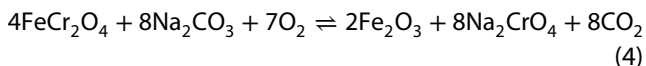
2.4 Recommended experimental procedures

2.4.1 Roasting of the chromite ore with Na_2CO_3

Antony et al. [26] and Zhang et al. [27] have been processed chromite ore by roasting with sodium carbonate, limestone and dolomite at 1000–1200 °C [27]. In the current study, the traditional method [26] was used for the recovery of chromate based chromite–Na_2CO_3 roast ore with sodium carbonate has been carried out with some modifications as follows:
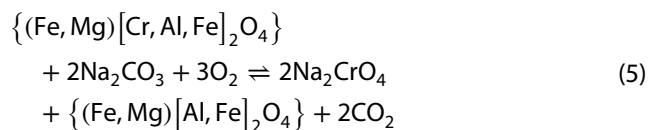
1. Four chromite samples (120–180 ± 0.01 g) were roasted with sodium carbonate in clay crucibles at about 1160 °C in air for 2 h. Iron in chromite roast reacts with sodium carbonate to produce $NaFeO_2$ + $NaAlSiO_4$ and other complex sodium-aluminium silicate according to the following reaction [1, 26]:

$$2FeCr_2O_4 + 1/2O_2 \rightleftharpoons 2Cr_2O_3 + Fe_2O_3 \tag{1}$$

$$2Cr_2O_3 + 2Na_2CO_3 \rightleftharpoons 2Na_2Cr_2O_4 + 2CO_2 \tag{2}$$

$$2Cr_2O_3 + 3O_2 + 4Na_2CO_3 \rightleftharpoons 4Na_2CrO_4 + 4CO_2 \tag{3}$$

Hence, the overall reaction can be expressed as follows:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightleftharpoons 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2 \tag{4}$$

Some other products e.g. $NaFeO_2$ + $NaAlSiO_4$ + other Na–Al silicates may be formed. The solid residue of roasting step was crushed and selectivity leached with water and/or or sulfuric acid until equilibrium. After leaching, the solid residues was quantitatively separated out from the water leachate. The recovery of Chromium(VI) as Na_2CrO_4 increased in the leachate on increasing the amount of Na_2CO_3 above the stoichiometric ratio demonstrated in the following equation [26]:

$$\{(Fe, Mg)[Cr, Al, Fe]_2O_4\}$$
$$+ 2Na_2CO_3 + 3O_2 \rightleftharpoons 2Na_2CrO_4 \tag{5}$$
$$+ \{(Fe, Mg)[Al, Fe]_2O_4\} + 2CO_2$$

2. The water leachate (liquor) was analyzed for major metal oxides, trace elements and PGMs using ICP-OES and/or ICP-MS. The un reacted chromium oxide remained in the chromite roast with the refractory oxides and ends up in the waste stream for landfills. ICP-OES analysis of the roast reduces after leaching was used to calculate the extraction yield according to the following equation:

$$\text{Extraction yield}\% = Cr_2O_3\% \text{ (in residue)}/Cr_2O_3\%\text{(in ore)} \times 100 \tag{6}$$

The percent yield of sodium chromate was also calculated by ICP-OES analysis of chromium in the leachate after leaching using the equation:

$$\%\text{Conversion yield of Cr} = Cr_2O_3\%\text{(liquor)}/Cr_2O_3\text{(ore)} \times 100 \tag{7}$$

3. After leaching the chromite roast with water, the solid residue was quantitatively separated out and digested with a mixture of concentrated $HClO_4$, HNO_3 and HF as reported [25]. The reaction mixture was heated slowly for 1 h at 100–150 °C on a hot plate. After the evolution of NO_2 fumes had ceased, the reaction mixture was evaporated almost to dryness. The solid residue was re-dissolved in HNO_3 (10.0 mL, 1.0 mol L^{-1}) and the resulting mixture was filtered through a Whatman 41 filter paper, transferred to volumetric flask (25.0 mL) and the solution was completed to the mark with deionized water and finally analyzed for major oxides, trace elements and PGM's using ICP-OES.

2.4.2 Influence of roasting time of the chromite ore with Na_2CO_3

In order to study the influence of roasting time of chromite ore with Na_2CO_3, an accurate weight (120–140 ± 0.01 g) of the chromite ore sample collected from Wadi Al Hwanet area (Sample I) were mixed well in clay crucible with an excess mass of sodium carbonate above the stoichiometric value in Eq. (1). The solid mixtures were roasted in muffle at about 1160 °C in air for various annealing time (2–6 h). The solid residues were left to cool and finally subjected to study the influence of leaching agent and contact time.

2.4.3 Influence of leaching agent and contact time of the chromite roast

The effect of various leaching agents e.g. boiled H_2O, HCl (1.0 mol L^{-1}) and H_2SO_4 (1.0–7.5 mol L^{-1}) and contact time
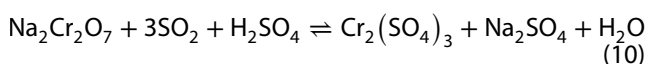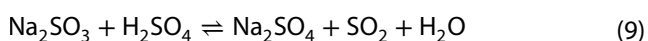
(4–10 h) on the recovery of Cr, Al, Ni, and PGEs was carried out on the chromite roasted at 5 h annealing time. The liquor (leachates) of each leaching agent at various contact time were critically filtered and finally analyzed for trace metal ions including Cr, Al, Fe and Ni oxides by ICP-OEs and ICP-MS for PGMs.

2.4.4 Preparation of basic chrome sulphate

The liquors containing Na_2CrO_4 obtained in the previous experiments were acidified with sulfuric acid to form $Na_2Cr_2O_7$ according to the following equation [27]:

$$2Na_2CrO_4 + H_2SO_4 + H_2O \rightleftharpoons Na_2Cr_2O_7 + Na_2SO_4 + 2H_2O \tag{8}$$
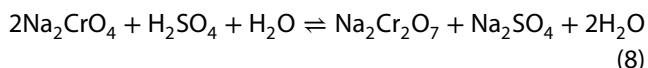
Basic chrome sulfate can then be manufactured by simple reduction of the resultant $Na_2Cr_2O_7$ in acid media to basic chrome sulfate with SO_2 according to the following equations:

$$Na_2SO_3 + H_2SO_4 \rightleftharpoons Na_2SO_4 + SO_2 + H_2O \tag{9}$$

$$Na_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightleftharpoons Cr_2(SO_4)_3 + Na_2SO_4 + H_2O \tag{10}$$

In a separate conical flask, the produced SO_2 gas from the reaction (9) was allowed to react with Na_2CrO_4 acidified with H_2SO_4 in another conical flask according to Eq. (10) to form basic chrome sulfate $Cr_2(SO_4)_3$ $(OH)_2$.

Upon evolution of SO_2 gas (Eq. 9), the aqueous acidified solution of Na_2CrO_4 is reduced in the second flask according to Eq. (10) to give a green and crystalline basic chrome sulfate after slow evaporation.

2.4.5 Extraction and recovery of PGMs

Extraction of the PGMs was performed following the recommended procedures reported earlier as follows: colloidal AuNPs solution was prepared as follows [28, 29]: In the present study, an accurate volume (500.0 mL) of sodium chromate water lechate of an accurate weight of the chromite roast with Na_2CO_3 was shaken well with MIBK (15.0 mL) in the presence of APDC (5 mL. 0.5% m/v) for 5 min. After equilibrium and layer separation, the organic phase was separated out. The PGEs were then stripped from the organic extract by shaking with 10 mL of HNO_3 (10 mL, 1.0 mol L^{-1}) containing $Hg(NO_3)_2$ (0.01% m/v) to form stable chelate with APDC and release other metal ions including PGMs. The PGE's in the organic phase was then stripped in the nitric acid layer and finally analyzed by ICP-OES and/or ICP-MS.

3 Results and discussion

3.1 Production of basic chromium sulfate

The chemical compositions of the four chromite ore samples collected from Wadi Al-Hwanet area (I, II, III) and Jabal Al Wasq (IV) are summarized in Table 1. The results were found comparable with the analyses of 41 chromite samples from Al'Ays ophiolite complex [28]. The content of Al_2O_3, Fe_2O_3, MgO and Cr_2O_3 oxides were found in the range 7–24%, 13–25%, 9–16%, and 44–68%, respectively in agreement with the data reported [28]. The relatively low level of SiO_2 (0.09–2.2%) in the reuse samples points to the low content of gangue silicate minerals which control

Table 1 Chemical analysis of the major oxides (wt%), trace metal and PGEs (µg g^{-1}) in the raw chromite ores

Oxide/element	I	II	III	IV
SiO$_2$	0.09	0.51	0.90	2.20
Al$_2$O$_3$	10.56	19.66	12.07	19.91
Fe$_2$O$_3$	12.96	12.04	11.78	09.78
MgO	17.38	20.85	17.81	17.04
Cr$_2$O$_3$	57.31	37.57	43.95	51.07
Ni	884	1626	2832	1125
Co	278	226	264	240
V	1240	1006	1080	1022
Cu	266	632	1116	103
Ti	1800	2900	1600	2240
P	1000	740	nd	1700
Mn	1600	2200	1300	1100
Pt	136 (113)	Nd (184)	25 (305)	63 (7)
Pd	nd (33)	nd (314)	nd (403)	678 (2)
Ru	nd (217)	nd (196)	nd (179)	nd (71)
Rh	nd (38)	nd (25)	nd (32)	nd (12)
Ir	Nd (57)	13 (56)	8 (66)	nd (51)
Os	nd (59)	nd (38)	nd (19)	nd (52)
Au	nd (10)	nd (47)	nd (33)	nd (nd)
Rh	nd (38)	nd (25)	nd (32)	nd (12)

ΣPGE's = 136 (519) 13 (813) 33 (1004) 741 (195)

Samples I–III were collected from Wadi Al Hwanet area

Sample IV was collected from Jabal Al Wasq area

Data in parenthesis were achieved by the fire assay NiS method and subsequently analysis by ICP-MS (µg kg^{-1}) Australia, µg kg

nd not detected

the sodium chromate yield which it can varies from 20 to 82% [26, 28].

Prichard et al. [28] have analyzed 41 chromite samples from Al'Ays ophiolite complex by Ni–sulfide fire assay method In that work, samples were properly digested with a mixture of $HF/HNO_3/HCl/HClO_4$ and analyzed by ICP-MS. The concentration levels of Pt, Pd, Ru, Rh, Ir and Os were in the range 3–2570; 4–6870; 41–5800; 5–840; 13–6200 and from 6 to 3300 µg/g, respectively. The ∑PGE's values are < 1 µg/g in 24 samples, from 1.0 to 3.0 µg/g in 14 samples, with two samples > 3 µg/g [28]. In the present study, the ∑PGM's of the studied four samples (I–IV) as analyzed by Gen analysis Laboratory, Australia were found comparable and are in acceptable agreement with the range reported from Al'Ays chromite [8, 28]. In this study, the high content of PGE's given in Table 1 may be ascribed to the nugget effect [30–33]. The heterogeneous distribution of the PGEs in the chromite samples may also account for this trend.

The percentage of unreacted chromite ore in the Na_2CO_3 roast after leaching with water varies between 59.81 and 86.63% as demonstrated in Table 2. This behavior is most likely attributed to: (1) The formation of Na_2CO_3–Na_2CrO_4 liquid phase which forms a thin film around chromite grains that inhibits diffusion of oxygen to the reaction interface [26] and (2) The large sizes of the crushed roast of small surface area. The percent of reacted chromite ore can be maximized by increasing the roasting time of chromite ore with Na_2CO_3 and also by raising the annealing temperature up to 1400 °C [26]. Antony et al. [26] have reported that, maximum percent formation and leaching of sodium chromate generally did not exceed 80–82%.

The results of chemical analysis of major oxides (wt%), trace elements and PGEs (µg mL^{-1}) of the water leach liquors of chromite roast are summarized in Table 3. The percent yield of Na_2CrO_4 in Table 3 is quite low as compared to the work of Antony et al. [26]. Thus, it can be concluded that, the roast residue in the present study can be considered as a lean ore and it may require further roasting time and high annealing temperature with Na_2CO_3 to convert most of the chromium oxide content in the chromite ore to sodium chromate [26]. In the roast, Na_2CO_3 reacts with Cr_2O_3 in the spinels forming sodium chromite ($Na_2Cr_2O_4$) as an intermediate phase which in turn is further oxidized in air producing sodium chromate (Na_2CrO_4). The grade content (%) of Cr_2O_3 of the chromite–Na_2CO_3 residue could further be improved by multiple stage consecutive preconcentration techniques, multi-gravity separator and high-intensity induced-roll magnetic separator [34].

Table 2 Major oxides (wt%), trace elements and PGEs (µg g^{-1}) contents of the chromite roast residues after leaching

Oxide/element	I	II	III	IV
SiO_2	00.09	2.40	0.04	0.19
Al_2O_3	05.07	9.65	11.96	5.3
Fe_2O_3	08.00	7.21	12.21	6.70
MgO	05.94	8.34	12.40	9.45
Na_2O	04.15	9.73	5.37	5.16
Cr_2O_3	17.37	21.61	38.13	30.19
Ni	512	1142	2758	775
Co	98	128	266	140
V	312	448	894	494
Cu	108	322	1070	227
Ti	1000	2020	1260	906
P	2800	946	00.00	906
Mn	800	1310	1400	950
Pt	nd	nd	18	2.42
Pd	nd	nd	nd	nd
Ru	nd	nd	nd	nd
Rh	nd	nd	nd	nd
Ir	nd	nd	10	nd
Os	nd	nd	nd	nd
Au	nd	nd	nd	nd

% Conversion = [Cr_2O_3 % (liquor)/Cr_2O_3 % (ore)]×100; *nd* not detected (below LOD)

Table 3 Results of chemical analysis of major oxides (wt.%), trace elements and PGEs (µg mL^{-1}) of the water leach liquors of chromite roast

Oxide/element	I	II	III	IV
SiO_2	0.02	0.26	0.02	0.20
Al_2O_3	0.70	0.36	0.64	0.04
Fe_2O_3	nd	nd	nd	nd
MgO	nd	nd	nd	nd
Na_2O	25.11	30.33	25.22	28.90
Cr_2O_3	4.03	0.97	2.69	3.00
Ni	884	1626	2832	1125
Co	278	226	264	240
V	1240	1006	1080	1022
Cu	266	632	1116	103
Ti	1800	2900	1600	2240
P	1000	740	0.00	1700
Mn	1600	2200	1300	1100
Pt	16	4	13	12
Pd	0.1	0.3	0.22	0.10
Ru	nd	nd	nd	nd
Rh	nd	nd	nd	nd
Ir	nd	0.26	0.10	0.11
Os	nd	nd	nd	nd
Au	1.95	0.5	1.35	1.59

% Conversion = [Cr_2O_3 % (liquor)/Cr_2O_3 % (ore)]×100; *nd* not detected
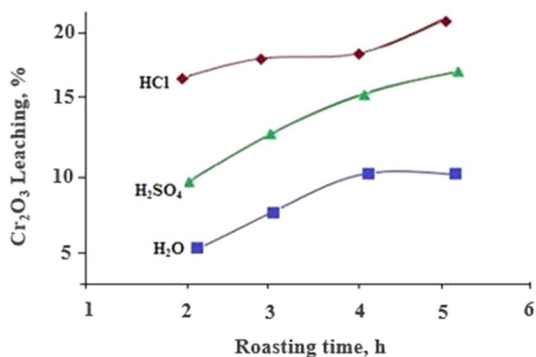
Fig. 1 Influence of roasting time (h) on the leaching of Cr_2O_3 from chromite roast by H_2O, H_2SO_4 and HCl at room temperature
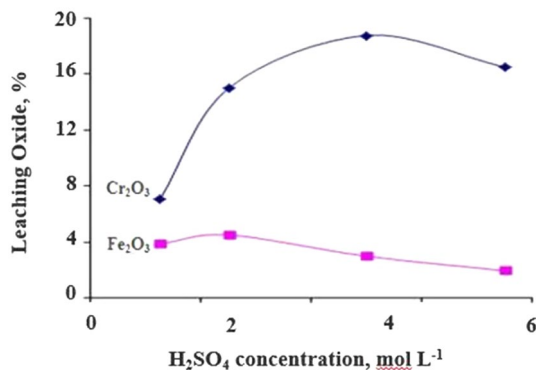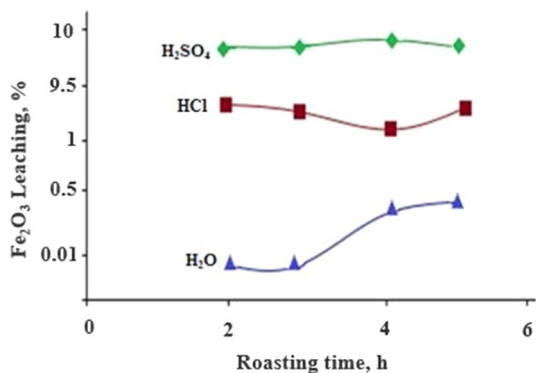

Fig. 2 Influence of roasting time (h) on the leaching of Fe_2O_3 from chromite roast by H_2O, H_2SO_4 and HCl at room temperature

Fig. 3 Influence of H_2SO_4 concentration on leaching of Cr_2O_3 and Fe_2O_3 from chromite–Na_2CO_3 roast
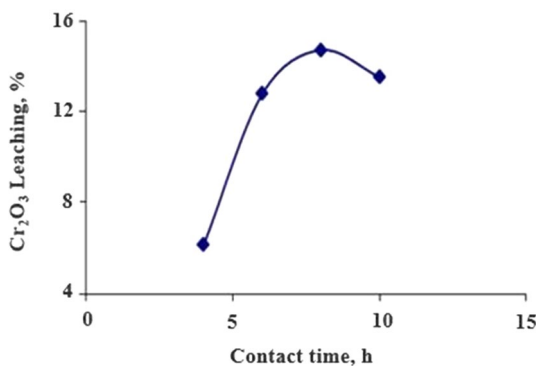

Fig. 4 Influence of contact time (hours) on Cr_2O_3 leaching by water at room temperature

In batch mode of separation, the effect of leaching time and temperature of the roasted chromite -Na_2CO_3 at different annealing ((roasting) time (2 to $\approx$ 6 h) on the extent of chromium and iron recovery as Cr_2O_3 and Fe_2O_3 was further conducted. In this experiments, a series of leaching agent's such as H_2O, HCl (1.0 mol L^{-1}), and H_2SO_4 (1.0 mol L^{-1}) were used. The influence of roasting time (2–6 h) on the extraction of Cr and Fe as Cr_2O_3 and Fe_2O_3 were critically investigated. After cooling, the chromite roast were shaken with the leaching agents (water, HCl, and H_2SO_4) for various time intervals and the resultant Cr and Fe in the leachates were analyzed by ICP-OES. The results for the extraction of Cr_2O_3 and Fe_2O_3 are shown in Figs. 1 and 2, respectively. The percentage yield of leached Cr_2O_3 (%) increased in the following order (Fig. 1): HCl > H_2SO_4 > H_2O whereas the leaching percentage of Fe_2O_3 followed the order (Fig. 2): H_2SO_4 > HCl > H_2O at room temperature. The leaching efficiency of Cr_2O_3 (%) using HCl (% Conv. Up to 39%) and H_2SO_4 (%Conv. Up to 36%) at concentration of 1.0 mol L^{-1} is greater than with H_2O (% Conv. Up to 26%) (Fig. 1).

The influence of H_2SO_4 and HCl concentrations (1.0–7.5 mol L^{-1}) individually on the leaching efficiency of Al_2O_3, MgO, Fe_2O_3 and Cr_2O_3 was carried out. Representative results using H_2SO_4 at various concentrations are shown in Fig. 3. The data revealed that, liquors produced by leaching with HCl and H_2SO_4 at different concentrations (0.5–7.5 mol L^{-1}) contain higher Cr_2O_3 and Fe_2O_3 compared with liquor produced by leaching with H_2O (Figs. 1 and 2).

The influence of contact time (4–10 h) on the leaching efficiency of Cr_2O_3 with water was critically carried out. The liquors were separated out and finally analyzed for chromium by ICP-OES. The leaching efficiency of Cr_2O_3 with water increases on increasing the contact time up to a maximum value after 8 h and leveled off at longer time as demonstrated in Fig. 4. The maximum value of tolerable Fe in the marketable basic chrome sulfate is 0.1%, whereas the present study provided leaching with water as a simple approach with cost-effectiveness for the production of high quality with good yield of basic chrome sulfate. Minimum iron content less than 0.1% required for the leather tanning industry was achieved in the present study. The

proposed study is also eco-friendly for the production of basic chrome sulfate and it gives a product nearly free from iron content when compared to the published methods. Thus, leaching with water is highly recommended for the production of basic chrome sulfate.

3.2 Production and extraction of PGM's

The composition of the water leach liquors of chromite roast (Table 3) reveals that, almost pure Na_2CrO_4 solution was achieved and most of the trace elements of the ore remained in the roast residue. The majority of the Ni content of the ore ends up in the chromite roast residue with values up to 0.4% NiO. The PGE's content of the ore was preconcentrated in the liquor because most of the PGEs form highly water soluble sodium salts e.g. sodium palatinate and some other sodium or potassium salts of PGEs [35]. The amount of PGEs remaining in the solid roast residues (minerals and alloys) are most likely enclosed within the un reacted chromite grains as demonstrated in Table 2.

The Na_2CrO_4 liquors obtained from roasting chromite ore with sodium carbonate was further acidified with H_2SO_4 to convert Na_2CrO_4 into $Na_2Cr_2O_7$ according to Eq. (8) and subsequently reduced with SO_2 gas prepared from reaction of Na_2SO_3 with dilute HCl (Eq. 9) to give basic chrome sulfate (Target compound in tanning industry) according to Eq. (10). The proposed method for basic chrome sulfate appears to be suitable for routine production of basic chrome sulfate. In conclusion, the proposed procedure could be utilized readily for routine production of the salt since the conventional methods in literature survey suffer from drawbacks e.g. high cost, multiple steps and are time consuming while the proposed method offers a simple system which is cost- effective, requires short analytical time coupled with good reproducibility, and nearly free from iron oxide content compared to the reported methods [26]. Na_2SO_4 is a part of the end product and it is not separated and remains as an inert diluent. The developed extraction method provided better separation, low cost and easy production of high grade basic chromium sulfate with less iron content as compared with the published methods [26].

3.3 Recovery of PGM's from chromite roast

Solvent extraction has a wide and well defined use in separation and/or preconcentration of PGMs from ores and solutions [36, 37]. The PGM's were enriched from the water liquor of sodium chromate by solvent extraction using APDC as a chelating agent and methylisobutyl ketone as extractant solvent. The fact that, the complexing agent APDC able to form stable chelates with PGMs according to the following equation:

$$M^{n+} + mAPDC \left[M(APDC)_m \right]_{org}^{n+} \qquad (11)$$
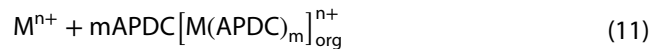
where M = PGMs and $M(APDC)_m]_{org}^{n+}$ is the precious metal complex in the organic solvent. The resultant PGMs were then stripped from the organic solvent by shaking with nitic acid solution contains mercuric ions. The results of the chemical analysis after solvent extraction and recovery of PGMs, Co, V and Ni are given in Table 4. These revealed better separation compared to other solvent extraction [38] and precipitation steps and precipitation methodology [39, 40]. The low level of the PGM's in the liquor is most likely attributed to the incomplete dissolution of the chromite ore, since; the un-converted ratio of chromite varies between 30 and 87% (m/m). The Na_2O content of the residue varies between 4.0 and 10.0% (Table 2). The high content of Na_2O in the residue is most likely attributed to the presence of excess Na_2CO_3 and/or inefficient leaching of Na_2CrO_4.

4 Conclusion and future perspectives

The present study provides a useful set of data on the production of basic chromium sulphate from chromite ore. The percent yield of sodium chromate is strongly dependent on the roasting time, particle size of roast, surface area, contact and shaking time, concentration and nature of leaching agent. Chromite dissolution during roasting with Na_2CO_3 s is variable and the percentage of the un reacted chromite lies in the range 30–87%. The remaining residue of the roast after leaching is rich in chromite which is considered as a lean ore and can be roasted again with Na_2CO_3 for further recovery of sodium chromate. The incomplete recovery of chromium is most likely attributed to formation of a binary Na_2CO_3–Na_2CrO_4 liquid during the roasting process which covers the chromite grains

Table 4 Chemical analysis of Ni, Co, V, and PGEs (Ir, Pd, Pt, Rh and Ru) ($\mu g/g^{-1}$) after solvent extraction and recovery with dilute nitric acid[†]

Oxide/element	I	II	III	IV
Ni	0.03	0.05	0.05	0.04
Co	0.06	0.05	0.04	0.11
V	0.46	0.50	0.26	0.82
Ir	3.80	4.37	2.64	3.89
Pd	nd	nd	nd	nd
Pt	0.27	0.16	0.12	0.46
Rh	nd	nd	nd	nd
Ru	nd	nd	nd	nd

nd not detected

and prevents the diffusion of oxygen and subsequently chromite dissolution. Basic chromium sulphate which is used in tanning industry is produced from the sodium chromate liquor after acidification with H_2SO_4 and reaction with SO_2. PGE's were collected in Na_2CrO_4 liquor while the majority of Ni (0.5% as NiO) was retained in the roast residue. Leaching with water offers a simple, an eco-friendly and cost-effectiveness approach for the production of a basic chromium sulfate product with high quality yield with minimum iron content (< 0.1% m/m) required for the tanning industry compared to the method reported [27]. Basic chromium sulfate product is nearly free from iron content when compared to the published methods. Thus, leaching with water is highly recommended for the production of basic chrome sulfate. PGMs were preconcentrated by liquid–liquid extraction using APDC as efficient complexing agent, recovered with HNO_3 and ICP-OES and/or ICP-MS analyzed. Work is continuing to conduct the roasting process at different temperature, extraction of Ni from roast residue, quantitative extraction and recovery of PGMs from chromate liquor and production of the target compound basic chromium. Work is ongoing for: (1) studying the roasting process at different temperature; (2) Studying the effect of particle size of the chromite ore and the crushed roast; Assigning the extraction and recovery of Ni from chromite roast residue and PGEs from the chromate liquor and finally (3) Production of the target basic chromium sulfate with low cost approach.

Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interests.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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