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The efficacy of flotation in beneficiating fine–ultrafine chromite from the UG2 tailings streams

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Abstract: South Africa produces platinum group metals (PGMs) from a UG2 ore that is also rich in chromite; the chromite is discarded as a tailings product. Since the fine dissemination of PGMs requires fine grinding to liberate the valuable metals, the products are in the fine-to-ultra-fine particle size range. The accumulation of valuable fines in tailings dams is a global phenomenon caused by a lack of adequate beneficiation methods for the fine material. Compared to gravity separation methods, flotation is more efficient for treating materials with particle sizes <100 microns but >25 microns. The current work explored the feasibility of floating chromite of -75/+25 microns and -25 microns in particle size. The zeta potential of a chromite concentrate is positive below pH 6 and negative above pH 6; the mineral liberation analysis of the UG2 tailings is reported. The investigated conditions included alkaline pH (8.5 to 10), collector dosage from 600 to 1000 g/t and four collector types. Flotinor-VF2711 and Collector-C showed great selectivity between chromite and silicates. The Cr_2O_3 grade was upgraded from ~12% to 20%; after one cleaning step, 25% Cr_2O_3 was achieved. The SiO_2 grade was reduced from ~37% to 24%. For the <25 μm fraction, direct flotation under the probed conditions did not yield results; reverse flotation is recommended for the treatment of the ultra-fine chromite sample.

Keywords: chromite, UG2 tailings analysis, chromite's zeta potential, chromite floatability, ultrafine beneficiation

1. Introduction

Platinum group metals (PGMs) are precious metals from which South Africa makes the majority of its mining income. Moreover, South Africa is a global leader in PGM production with 80% of global PGM reserves. Currently, PGMs are produced from the Upper Ground 2 (UG2) reef, where sulphides host PGMs, with silicates and chromite as the main gangue minerals. PGMs are beneficiated through flotation, where sulphides are collected as a concentrate while the silicates and chromite are depressed to the tailings stream. Due to the fine dissemination of PGMs in the ore, tertiary grinding is necessary to achieve liberation; as such, the flotation products have very fine particle sizes (Wesseldijk et al., 1999; Song et al., 2018; Thethwayo, 2018). Chromite is the main source of chromium metal, which is a very important ingredient in the ferro-alloy industry for the production of stainless steel, among other uses (Gallios et al., 2007; Dawson, 2010; Murthy et al., 2011; Deniz, 2020). For chromium production, the desired Cr_2O_3 grade is >40% (Dawson, 2010; Deniz, 2020). A typical Cr_2O_3 grade in the UG2 tailings product ranges from ~10 to ~20 weight % (wt. %) Cr_2O_3; to be economical, it must be upgraded to >40% Cr_2O_3. The benefit of recovering chromite from the PGM flotation tailings is twofold:

- it prevents the loss of valuable minerals to the tailings dam while preventing possible leaching of the chromite to chromium VI, which is a carcinogen (Escudero-Castejón et al. 2021); and
- the tailings serve as a secondary source of chromite, which alleviates the costs and impact of mining virgin materials (Khakmardan, et al. 2020, Ozun et al. 2025)

Chromite is of the spinel group containing Al, Cr, Fe and Mg, with the balance being oxygen. It is a solid solution, which is stable over a range of compositions from iron-rich ($FeCr_2O_4$) to magnesia-rich

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($MgCr_2O_4$). As such, the typical chromite formula can be presented by (Fe^{2+}, Mg)(Cr, Al, Fe^{3+})$_2$O$_4$ (Murthy et al. 2011). The variability in chromite mineralogy influences its properties; its density varies from 4.5 to 5 g/cm^3, and the surface properties vary depending on the concentration of each element in this compound. The gangue minerals associated with chromite are pyroxene [$(Mg,Fe)Si_2O_6$], olivine [$(Mg,Fe)_2SiO_4$] and serpentine [$(X)_3Si_2O_5(OH)_4$], where X can be Al, Fe or Mg, and in rare cases, Mn, Ni or Zn (Deniz, 2020). The surface properties of these silicates depend on the dominant elements, while the density and hardness vary from ~3.2 to ~3.6 g/cm^3 and 5 to 7, respectively. Gravity separators are well-suited for separating chromite from silicates given their density differences; however, at particle sizes less than 100 microns, the efficiency of gravity and magnetic separators is impaired (Feng and Aldrich, 2004; Tamam and Seifelnasr, 2012). The fineness of the PGM flotation tailings (<75 microns) limits the application of the conventional methods in efficiently separating the chromite from the silicates (Gallios et al., 2007; Murthy et al., 2011). The current work probed an efficient method to upgrade a low-grade tailings product to a Cr_2O_3 grade of >40%. Flotation is reportedly the most efficient method for beneficiating the materials of particle sizes <75 microns (Murthy et al., 2011; Tamam and Seifelnasr, 2012).

The floatability of chromite has been the subject of several studies (Gallios et al., 2007; Tamam and Seifelnasr, 2012; Deniz, 2020; Guven et al., 2022; Ross et al., 2022). The pH, collector type, collector dosage and activator are the main determining factors in the floatability of chromite (Deniz, 2020). The floatability of chromite is feasible under both acidic and alkaline conditions, depending on the collector type and dosage; however, selecting collectors for separating chromite from silicates is challenging since these minerals may assume similar surface properties under certain conditions (Gallios et al., 2007). Under alkaline conditions (pH 8 to 11), the selectivity of chromite is reportedly favourable with the addition of a silicate depressant (Tamam and Seifelnasr, 2012; Guven et al., 2020). However, the optimum pH for selectivity is associated with the collector type and collector dosage (Gallios et al., 2007; Turri et al., 2017; Cook and Gibson, 2023). For oxide mineral flotation, amines as cationic collectors, and fatty acids and sulphonates as anionic collectors are reportedly efficient. For chromite flotation at both alkaline and acidic pHs, the efficiency of the listed collector types depends on the pH modifier used (Yiğit et al. 2014; Turri et al., 2017).

Guven et al. (2020) reported that at pH 8.48, increasing the collector dosage affects the zeta potentials of both the chromite and the silicates. At lower collector concentrations, the chromite could be selectively floated; when the collector concentration increased, the zeta potentials of both the chromite and the silicate changed from positive to negative. The silicates became more negative with the increase in collector concentration, thereby hindering the selectivity of the collector (Guven et al. (2020). The dissolution of cations on the chromite particles' surface further exacerbates the phenomenon of chromite response to pH and collector variability. This presents a challenge for predicting chromite selectivity in flotation (Güney et al., 1999; Escudero-Castejón et al., 2021). For a South African chromite ore, Yiğit et al. (2014) successfully upgraded a UG2 chromite from 30% to ~40% Cr_2O_3 at pH 1 to 3 after three cleaning steps. They used an untreated, high-grade UG2 sample (Yiğit et al., 2014). Data on the treatment of low-grade tailings chromite samples are scarce; the inter-effects among collector type, collector dosage and pH on low-grade chromite floatability have rarely been reported. Although the zeta potential is negative for both chromite and silicates above pH 6, it is desirable to float under alkaline conditions, since acidic conditions can be corrosive to the equipment.

The current investigation focused on elucidating the feasibility of selectively floating low-grade, fine chromite while depressing silicates at alkaline conditions. The sensitivity of chromite floatability to collector type, collector dosage, flotation time and pH was probed.

2. Materials and methods

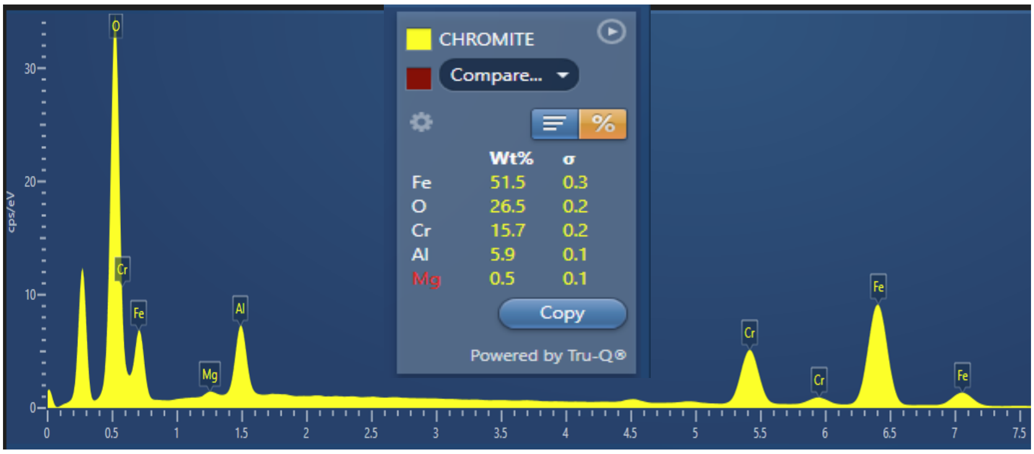
2.1. The characterisation of the chromite sample

A UG2 flotation tailings sample was acquired from a local concentrator, where the UG2 ore had undergone a Mill-Float/Mill-Float circuit to extract the sulphides with PGMs and discard chromite and silicates as tailings. Using a hydro-cyclone, the sample was de-slimed at 25 microns to separate the (+25 µm) from the (-25 µm). Initially, the flotation tests were conducted on the +25 µm fraction to determine the optimal conditions; the -25 µm fraction was floated at the best conditions determined for the +25 µm fraction. The elemental and phase composition of the sample was achieved using scanning electron microscopy (SEM), mineral liberation analysis (MLA), X-ray diffraction (XRD), and X-ray fluorescence (XRF).

2.1.1. SEM analysis

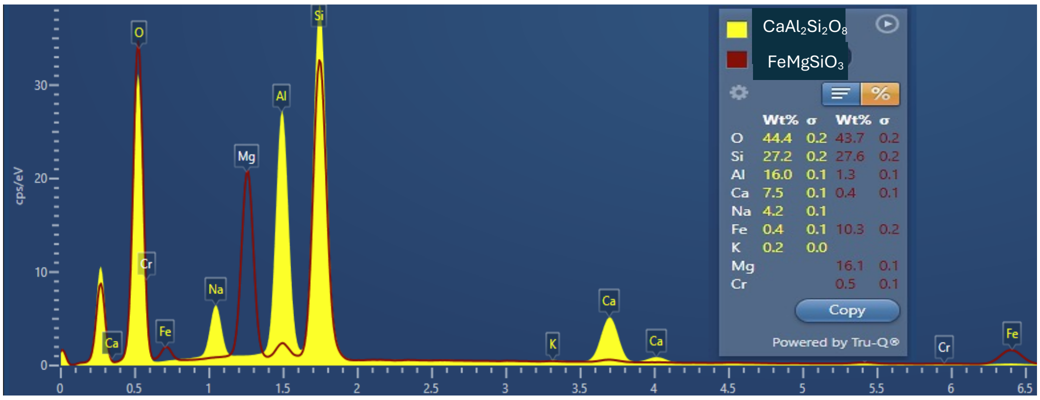
For SEM analysis, the aliquot sample was mounted in resin, polished and coated with carbon, after which it was analysed using a JEOL-7900F fitted with an Oxford-Aztech crystal. The scanning electron microscope was equipped with electron dispersive X-ray spectroscopy (EDS) and backscattered electron (BSE) image detectors. The chromite and silicates SEM-EDS spectra are displayed in Figs. 1 and 2, respectively. The iron-rich chromite [$Fe(Cr,Al)_2O_4$] was dominant, while the prominent silicates were the magnesia-rich silicate and calcium-alumina. The EDS spectra of the two silicate phases are superimposed in Fig. 2 to emphasise the contrast in their composition, as this could present varied flotation responses.

The SEM-X-ray mapping was acquired to ascertain the topography of the phases and confirm the association of the species; the images are depicted in Fig. 3. The suggested phases are not stoichiometric representations of the phase; they are the detected elements over the analysed area. The "C" detected in all the images emanates from the carbon coating used in sample preparation. In Fig. 3, a) is a BSE image, which represents the area of analysis, and b) is an iron-rich chromite phase, which was also detected in the SEM-EDS spectrum in Fig. 1. Fig. 3 c), d) and e) are silicate phases, two of which were detected as magnesia-rich silicate and calcium-alumina silicate in Fig. 2. Both the EDS and X-ray maps confirm the presence of Al, Fe and Mg in both the chromite and the silicates. The Cr_2O_3 was then used as a measure of chromite grade, while the SiO_2 was used as a quantitative measure of silicates, since all the other oxides associated with both the chromite and the silicates, except CaO, which was in minor amounts.



	Wt%	σ
Fe	51.5	0.3
O	26.5	0.2
Cr	15.7	0.2
Al	5.9	0.1
Mg	0.5	0.1

Fig. 1. SEM-EDS spectrum of the as-received UG2 sample, showing the chromite phases spot analysis



	Wt%	σ	Wt%	σ
O	44.4	0.2	43.7	0.2
Si	27.2	0.2	27.6	0.2
Al	16.0	0.1	1.3	0.1
Ca	7.5	0.1	0.4	0.1
Na	4.2	0.1		
Fe	0.4	0.1	10.3	0.2
K	0.2	0.0		
Mg			16.1	0.1
Cr			0.5	0.1

Fig. 2. SEM-EDS spectrum of the as-received UG2 sample, showing the silicate phases ($FeMgSiO_3$) and ($CaAl_2Si_2O_8$) spot analysis

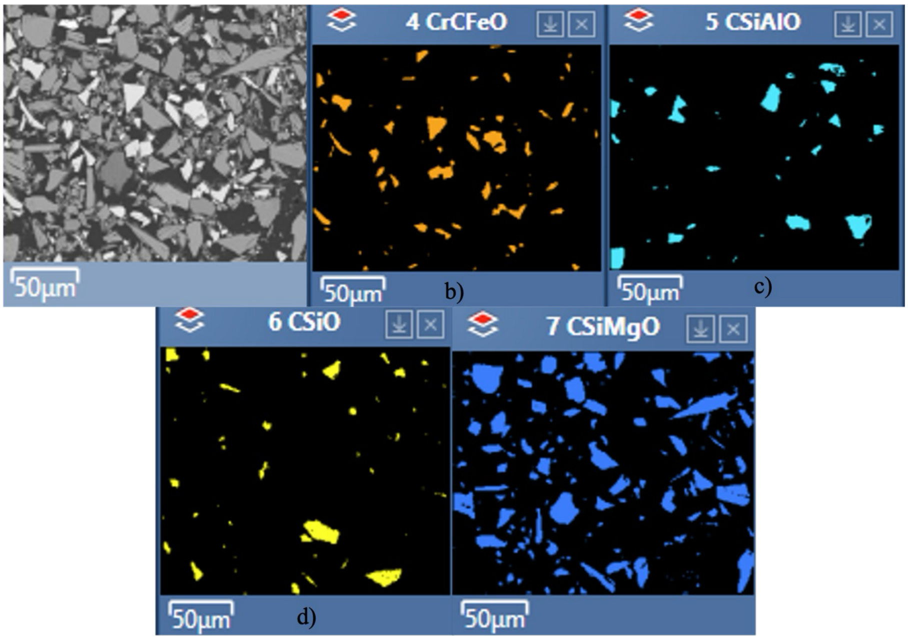


Fig. 3. SEM-X-ray elemental mapping of the as-received UG2 sample, a) backscattered electron image, b) iron-rich chromite, c) alumina silicate, d) silica, e) magnesia silicate

2.1.2. Mineral liberation analysis

MLA was conducted on the as-received sample to determine the degree of liberation and confirm the chemical phases detectable in the sample. A single 30 mm diameter cast resin stub was produced, consisting of 0.5 grams of the sample mixed with 0.2 grams of graphite. This cured stub was halved, turned and recast to present a cross-section of the original cast stub. This stub was polished and coated with carbon. The prepared, polished stub was scanned using an ASPEX scanning electron microscope with a Bruker EDS system controlled by the MLA software suite.

The phases, formulae and elemental composition of each phase are depicted in Table 1. Magnesia-rich chromite was a major chromite phase present in the sample, noteworthy is the presence of silicon in the chromite-calcium. Calcium aluminium silicate and iron magnesia silicate were prominent silicates detected by MLA; these phases were also detected by SEM, as displayed in Figs. 1 to 3. Hydrated silicates were detected in minor amounts. The degree of liberation and the quantitative analysis of the phases are depicted in Table 2. The particle size fraction was classified into -10 µm, (+10/-150 µm) and +150 µm. The liberation analysis is reported for the (+10/-150 µm) fraction, as this is deemed the ideal flotation size range. It is acknowledged that agglomeration can occur during sample preparation; therefore, the particle size distribution and the degree of liberation may incur some errors. The chromite seemed to be less liberated, with an average 50% liberation of the (+10/-150 µm) fraction, which would pose challenging for selective flotation. The silicates had a higher degree of liberation of >80%, which would improve selectivity since silicate response would be less impaired than that of chromite. Due to the nature of the analysis, the topography of the locked particles could not be acquired to ascertain the association of locked particles. Albeit the SEM-BSE images and X-ray mapping of the selected areas did not indicate any locked phases.

2.1.3. Zeta potential analysis

To determine the zeta potential of the components of the UG2 tailings sample, the +25 µm fraction was further screened to separate the (+53/-75 µm) fraction, which was treated using a shaking table. The shaking table was used to create a chromite-rich concentrate and a silicate-rich tailings. These shaking table products were then analysed using a zeta-meter to determine the surface charges of chromite and silicates as a function of pH. The (+53/-75 µm) fraction was easier to concentrate by shaking; the -53 µm fraction was excluded since the shaking table could not efficiently concentrate this finer size fraction. The XRF analysis of the as-received feed and the (+53/-75 µm) shaking table products is displayed in Table 3.

Table 1. Mineral liberation (qualitative) analysis of the as-received UG2 flotation tailings sample (elemental analysis in weight %)

Name	Formula	Al	Ca	Cr	Fe	Mg	Na	O	Si	Ti
Chromite	$(Fe_{2+}, Mg)(Cr,Al)_2O_4$	8	0	32	22	4	0	32	0	1
Chromite-Ca	$(Fe_{2+}, Mg)(Cr,Al)_2O_4$	5	3	14	17	10	0	38	13	0
Chromite-Ti	$(Fe_{2+}, Mg)(Cr,Al)_2O_4$	6	0	27	33	3	0	30	0	1
Fe-oxide	$Fe_2^{3+}Fe^{2+}O_4$	0	0	0	72	0	0	28	0	0
Pyroxenes (enstatite)	$(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$	5	15	0	5	9	1	41	23	2
Plagioclase (anorthite)	$Na_{0.5}Ca_{0.5}Si_3AlO_8$	10	7	0	0	0	4	47	31	0
Actinolite	$Ca_2Mg_3Fe^{2+}{}_2Si_8O_{22}(OH)_2$	1	9	0	9	10	1	35	35	0
Mica	$KMg_{2.5}Fe^{2+}{}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$	6	0	0	6	14	0	43	19	0
Silicates		0	0	0	0	0	0	53	47	0
Other minerals (olivine)		0	0	0	15	25	0	42	18	0

Table 2. Mineral liberation (qualitative) analysis of the as-received UG2 flotation tailings sample (degree of liberation)

		>150 µm	<10 µm	+10/-150 µm	*liberated	*locked
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
Chromite	17.1	1	24	75	42	34
Chromite-Ca	4.6	2	36	62	18	44
Chromite-Ti	14	1	20	79	36	42
Fe-oxide	2.1	48	11	41	21	20
Pyroxenes	32.1	16	11	73	62	11
Plagioclase	21.9	9	13	78	69	10
Actinolite	4.2	2	18	80	46	34
Mica	1.1	12	11	77	69	8
Silicates	2	11	19	70	57	14
Other minerals	1.1	1	18	81	51	30

*liberated or locked refers to the +10/-150 µm fraction, which is deemed the ideal flotation size range

wt. %: weight %

The Cr_2O_3 and SiO_2 contents were evaluated as these represent the minerals of interest—chromite and silicates, respectively. The Cr_2O_3 in the feed was ~12%, while the SiO_2 was 36%. The shaking table upgraded the Cr_2O_3 from 12% in the feed to 40% in the concentrate; the concentrate still had about 4% SiO_2. In the shaking table tailings, the SiO_2 increased from 36% in the feed to 42.9%, and the tailings still had ~6% Cr_2O_3, which was deemed minimal. The shaking table concentrate and tailings were each analysed to ascertain the zeta potential of the chromite and silicates.

The zeta potential measurements were determined using an Anton Paar zeta-meter. Deionised water was mixed with the solids at a solids/liquid ratio of 0.0005. NaOH and HCl were used to achieve the target alkaline and acidic pHs, respectively. After achieving the target pH for each aliquot solution, each sample was homogenised in an ultrasonic bath before testing. Zeta potential as a function of pH is displayed in Fig. 4.

The chromite's zeta potential was positive from pH 1 to 5, after which it became negative from pH 6 to 11. This data aligns with the findings of Deniz. (2020), who observed that the zeta potential of chromite switches from positive to negative at pHs below 6. Under strong acidic conditions, the dissolution of particles and the presence of cations interfere with the particle charge and complicate the surface properties (Gallios et al. 2007; Guven et al., 2020; Ross et al., 2022). The instability or variation of the charge at pHs below 3 may be attributed to the effect of high acidic conditions on the surface charge, as well as the complex mineralogy of chromite, where elements like Al, Fe and Cr may interchangeably dominate the particle charge. The silicates had a slightly positive zeta potential from pH 1 to 2, while above pH 2, throughout the pH range, they had a negative zeta potential.

Based on the zeta potentials of chromite and silicates, chromite could be selectively floatable between pH 2.5 and pH 5 using cationic collectors. Above pH 6, selectively floating chromite and rejecting silicates is challenging due to the similar charges exhibited in Fig. 4. The current flotation work was carried out in alkaline conditions, driven by the available collectors and the industry's inclination towards natural pH rather than acidic conditions.

Table 3. XRF analysis of the as-received UG2 flotation tailings sample and the shaking table products of the +53/-75 µm fraction

Oxide (wt. %)	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3	MgO	SiO_2	Other
Feed	7.3± 1	4.1± 0.4	12.1 ± 2	22± 7	16.4 ± 4	36.1± 3	2
Shaking table concentrate	9.1	0.4	40	37.8	5.1	4.2	3.4
Shaking table tailings	6.9	5.4	5.6	20.9	16.1	42.9	2.1

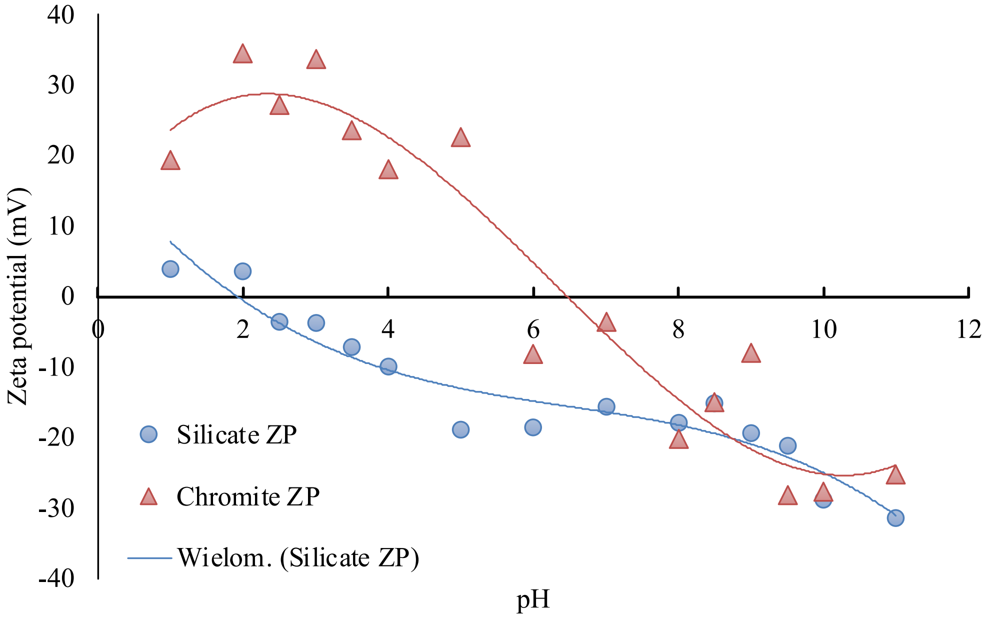


Fig. 4. Zeta potential as a function of pH for chromite (shaking table concentrate) and silicates (shaking table tailings)

X-ray diffraction analysis

The shaking table concentrate and tailings were subjected to XRD analysis to ascertain the crystalline phases present in the sample. For the XRD analysis, the material was prepared using a backloading preparation method. Diffractograms were obtained using a Malvern Panalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe-filtered Co-Kα radiation. The phases were identified using X'Pert Highscore Plus software. The relative phase amounts (wt. %) were estimated using the Rietveld method. The XRD diffractograms are appended as Figs. A1 and A2.

The shaking table concentrate had ~84 wt. % ferromagnesia chromite with the silicates amounting to ~16 wt. %. The shaking table tailings had ~91 wt. % silicates and ~9 wt. % chromite. Magnesia-rich silicate (enstatite) and calcium-alumina silicate formed the bulk of the gangue minerals; these phases were also detected by the MLA (Table 1) and SEM (as depicted in Figs. 2 and 3).

2.1.4. Flotation tests

The (+25/-75 µm) fraction of the UG2 flotation tailings was treated with a flotation process to ascertain the efficacy of flotation in upgrading the grade of chromite. The effects of collector type, collector dosage, flotation time and pH on selective chromite floatability were investigated.

2.2. Reagent suit

Four collectors were selected based on availability and supplier baseline data:
- Betacol-175 (supplied by Betachem)
- Flotinor-VF2711 (supplied by Clariant)
- Lupromin-476 (supplied by BASF)
- Collector-C (In-house)

Betacol-175 is a fatty acid-based anionic collector, and Lupromin-476 is a fatty acid mixture of 22% oleic acid and 57% linoleic acid with some chemical additives (Budemberg et al., 2019). Flotinor-VF2711 is an amine-based anionic collector (de Medeiros and Baltar, 2018; Ross et al., 2022). Collector-C is a combination of ricinoleic, oleic and linoleic acids. Dowfroth 200 was used as a frother, and lime was used as a pH modifier. The silicate depressant was not added in the main test. Carboxymethyl cellulose (CMC) was only added during the cleaning stages to depress the silicate gangue minerals.

3. Experimental conditions

The flotation tests were classified into three sets. The first set was to determine the optimum pH and collector dosage at which the highest Cr_2O_3 grade can be achieved; these were tested using two collectors (Flotinor-VF2711 and Collector-C). The optimum pH and collector dosage from set 1 were used in set 2 to determine the best collector, comparing four collectors. The last set of experiments (set 3) was to determine the efficacy of flotation in floating <25 µm particle size chromite. The conditions tested were based on the pH, collector dosage, and flotation time determined from sets 1 and 2. The tested collectors were Flotinor-VF2711 and Collector-C.

For each test, a 500-gram sample was mixed with 1.8 litres of deionised water in a 2.5 L Denver cell. The slurry was agitated at a rotation speed of 1200 rpm, and the air rate was monitored based on the froth stability. After adding the collector, the pH of the slurry was modified accordingly. After adding a frother, the air was opened to initiate the test. The concentrate was collected every two minutes at 10-second intervals. The flotation time was fractioned into two and four minutes. At the end of the test, the products were dried, weighed and analysed. XRF was used to determine the elemental composition of the products, mostly focusing on the Cr_2O_3 and SiO_2 grades. The data were analysed with the Minitab response surface methodology (RSM) to determine the optimal collector dosage and pH to produce a concentrate with the maximum Cr_2O_3 grade and the minimum SiO_2 grade.

3.1. The recovery of chromite as a function of pH and collector dosage

Collector-C and Flotinor-VF2711 were initially tested to determine the optimal conditions for yielding maximum chromite and minimum silicate without a depressant. The pH varied from 8.5 to 10, the collector dosage varied from 600 to 1000 g/t, and the flotation time varied from two to four minutes to limit collecting silicates to the concentrate. After four minutes, the test was stopped, and the residual pulp was allowed to settle in a flotation cell. The images of the residual pulp for both collectors are depicted in Fig. 5. The tailings settled at the bottom of the cell, but an accretion remained suspended above the residual solution. The accretion was skimmed and named "last" concentrate. Each concentrate (two minutes, four minutes and last concentrate) was analysed separately to ascertain the elemental composition and the particle size distribution. XRF was used to determine the grades of the products, and microtrac-Malvern Mastersizer 2000 was used to determine the PSD of the products.

3.2. The efficacy of four collectors on chromite recovery

The optimum conditions from experimental set 1 were used to determine the efficacy of four collectors, i.e., Betacol-175, Flotinor-VF2711, Lupromin-476 and Collector-C. The collector dosage was constant at 1000 g/t, the pH was 9, and the flotation time was varied to two, four and six minutes. Increasing the flotation time to six minutes aimed to collect the slow-floating concentrate. A single cleaning stage was conducted at pH 9 with 1000 g/t of Collector-C and the addition of 100 g/t CMC depressant. A depressant was added to suppress the gangue and subsequently improve the grade of Cr_2O_3 in the final concentrate.

3.3. The floatability of a -25 µm tailings sample

To probe the floatability of the -25 µm fraction, the best conditions from the preceding experiments were used, i.e., Collector-C and Flotinor-VF2711 were tested in the absence of a depressant at a constant dosage of 1000 g/t, a pH of 9, and the flotation time was two, four and six minutes.

4. Results

4.1. The recovery of chromite as a function of pH and collector dosage

Flotinor-F2711 and Collector-C were tested at various pHs (8.5 to 10) and collector dosages (600 to 1000 g/t). At the end of each test, the residual pulp was allowed to settle; the Flotinor-VF2711 and Collector-C residual products are depicted in Fig. 5. The residue segregated into three layers: the solid tailings, which settled at the bottom; the solution; and the accretion, which was suspended above the solution. The morphology of the accretion differed with the collector used. For Flotinor-VF2711, the finest particles segregated just above the solution and a coarser, frothy, greyish layer rested on the fines layer. For Collector-C, the accretion had no distinct layering but rather a mushy layer that rested atop the solution. To determine the mechanism behind the morphology of the residual float, all the products and feed were subjected to PSD analysis. The PSD curves of the feed and the flotation products for Flotinor-VF2711 and Collector-C at pH 9 and a collector dosage of 1000 g/t are depicted in Figs. 6 and 7, respectively. F1, F2 and F-L in Fig. 6 correspond to the Flotinor-VF2711 concentrates collected after two minutes, four minutes, and the residual accretion, respectively. Feed F and F-Tail are the feed and the tailing PSD, respectively. C1, C2 and C-L in Fig. 7 correspond to the Collector-C concentrates collected after two minutes, four minutes, and the residual accretion, respectively. Feed C and C-Tail are the feed and the tailing PSD, respectively.

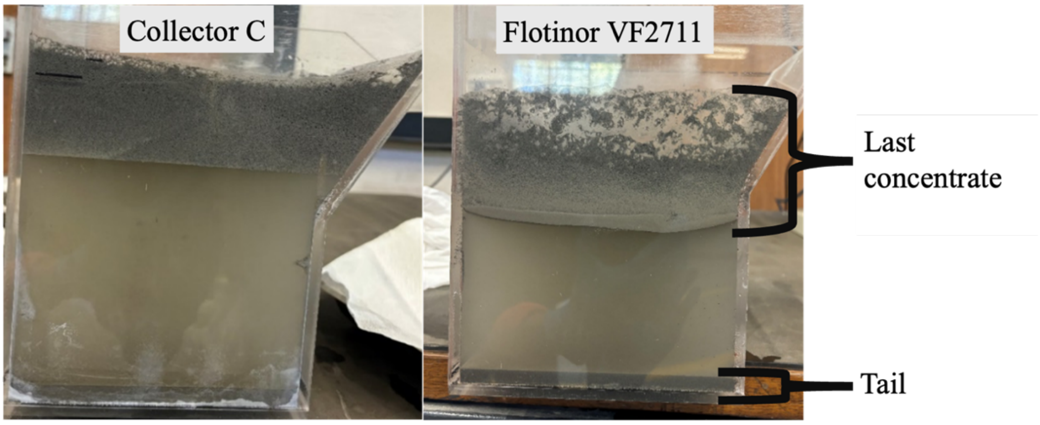


Fig. 5. The morphology of the residual pulp after four minutes flotation time, showing Collector-C (left) and Flotinor-VF2711 (right); the top accretion is the Last concentrate, the bottom sediment is the tailings

RSM was used to study the interaction effects of the collector dosage, pH and flotation time on Cr_2O_3 grade. For set 1, Flotinor-VF2711 and Collector-C showed comparable results; the Cr_2O_3 grade had a variance of less than 1% at the pH and dosage ranges tested. Increasing the pH from 8 to 9 yielded the highest Cr_2O_3 grade of 18.3% and a low SiO_2 of 29.96%. Increasing the pH beyond 9 depressed the Cr_2O_3 grade and enhanced the SiO_2 grade. At low collector dosages, the Cr_2O_3 grade increased with flotation time; however, the high dosages of 1000 g/t yielded a higher Cr_2O_3 grade, and the grade decreased with time as silicate recovery increased at high dosages. Based on the RSM analysis, the optimal pH was 8.89, while the optimal dosage was 1000 g/t. The Cr_2O_3 grade increased from a pH of 8.5 to a pH of 9, after which it dropped when the pH was increased to 10. The optimal flotation time was two minutes, where a Cr_2O_3 grade of 19.9% was achieved, with a SiO_2 grade of 27.4%. As the flotation time increased beyond two minutes, the Cr_2O_3 grade decreased in favour of the SiO_2 grade. The best collector dosage and pH were then concluded to be 1000 g/t and a pH of 9, respectively.

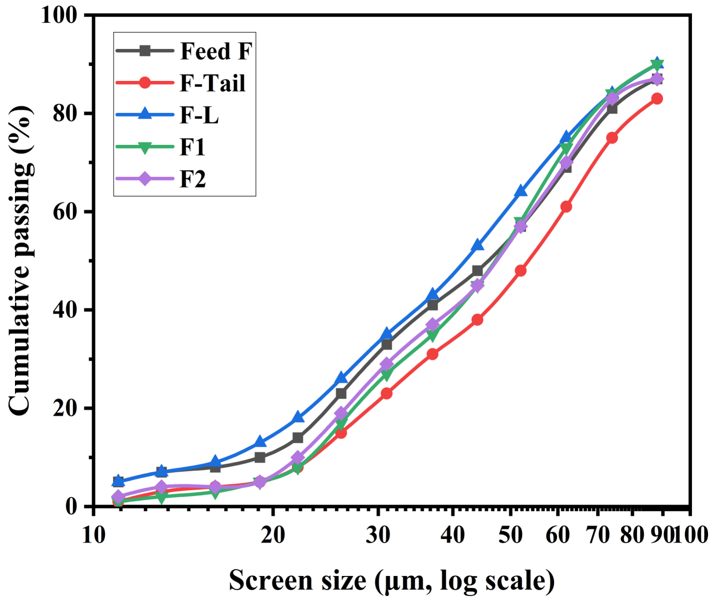


Fig. 6. Particle size distribution of the Flotinor-VF2711 flotation products

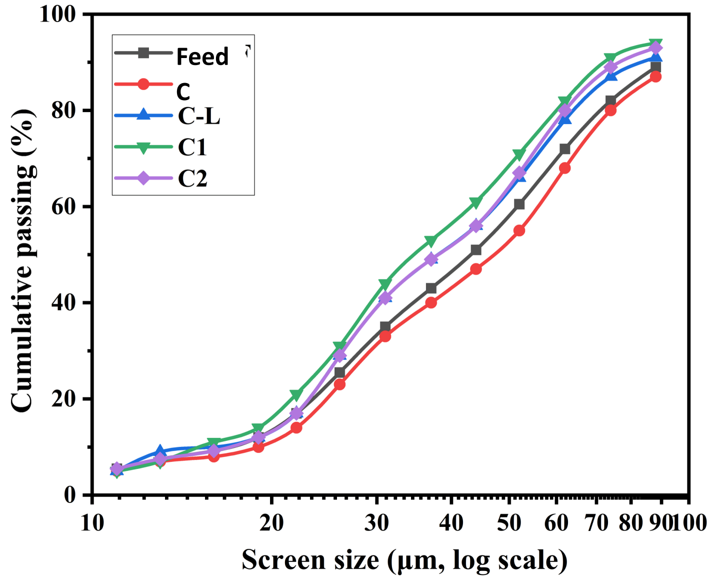


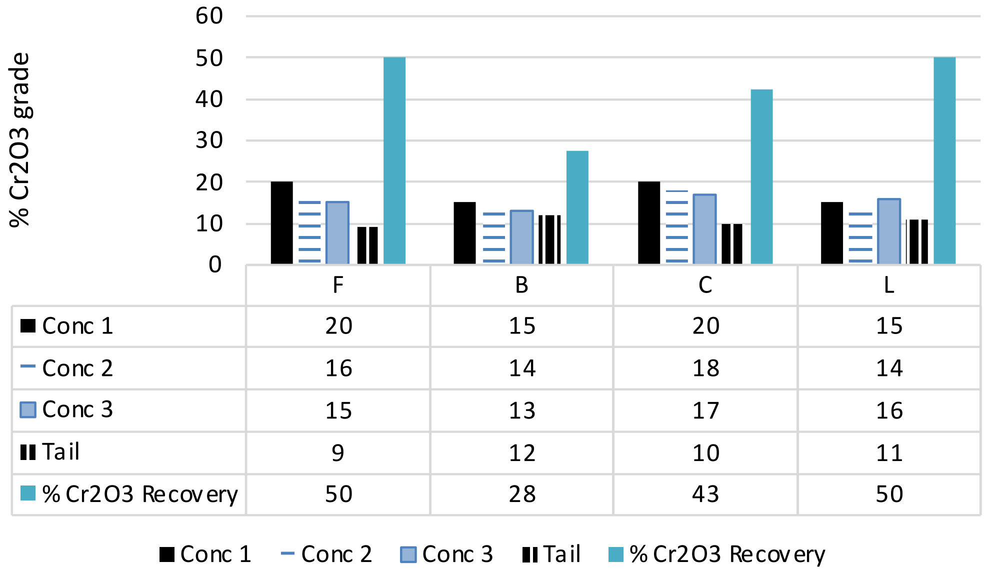
Fig. 7. Particle size distribution of the Collector-C flotation products

4.2. The efficacy of four collectors

The efficacy of four collectors for the selective flotation of chromite was tested at a constant pH of 9 and a collector dosage of 1000 g/t, with the concentrates collected for two, four and six minutes. The products were analysed for Cr_2O_3 and SiO_2 grade. The data shown in Fig. 8 depict Cr_2O_3 % grade and recovery as a function of the collector type, while Fig. 9 depicts the mass pull %. Flotinor-VF2711 and Collector-C had a comparable effect on Cr_2O_3 floatability; at two minutes, a Cr_2O_3 grade of ~20% was observed, with the Cr_2O_3 recovery of 50 and 43% respectively, the on Cr_2O_3 grade declined with flotation time. Betacol-175 and Lupromin-476 reached a highest Cr_2O_3 grade of 15% after two minutes. With Betacol-175, the on Cr_2O_3 grade declined slightly with flotation time, while Lupromin-476 exhibited 16% Cr_2O_3 grade at six minutes flotation time. The slight increase in Cr_2O_3 grade with Lupromin-476 could be attributed to the mass pull, which was significantly lower compared to the first four minutes of flotation time, possibly because most of the pulp had floated, which made Cr_2O_3 appear to increase.

The mass pull % of Flotinor-VF2711 increased with flotation time, while that of Collector-C decreased, as depicted in Fig. 10. This is an intriguing observation since the PSD results of products in Figs. 6 and

7 show that the flotation mechanisms for these collectors are different. While Flotinor-VF2711 preferentially floated the coarser fraction, Collector-C floated fines such that all the concentrates were finer than the feed. The preferential particle size and the trend observed with the mass pull % are potentially influenced by a similar effect, such as the particle-bubble adhesion mechanism. The best collector was Collector-C based on its average Cr_2O_3 and SiO_2 grades over time. Flotinor-VF2711 had comparable results to Collector-C; however, Collector-C maintained a low SiO_2 grade even with increasing flotation time.



	F	B	C	L
Conc 1	20	15	20	15
Conc 2	16	14	18	14
Conc 3	15	13	17	16
Tail	9	12	10	11
% Cr2O3 Recovery	50	28	43	50

Fig. 8. Cr_2O_3 % grade as a function of collector type and flotation time; Conc 1, Conc 2 and Conc 3 are concentrates collected after two, four and six minutes, respectively

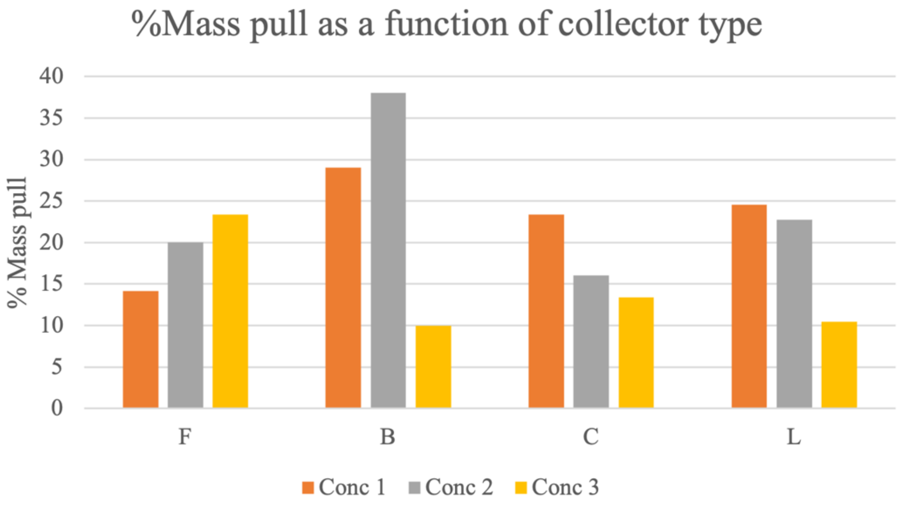
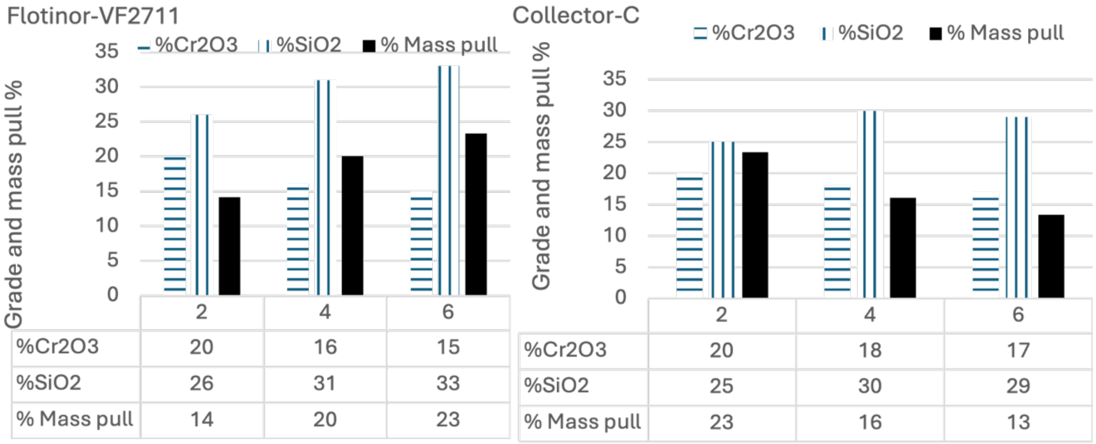


Fig. 9. Mass pull % as a function of collector type and flotation time; Conc 1, Conc 2 and Conc 3 are concentrates collected after two, four and six minutes, respectively

A single cleaning stage was conducted on the concentrate produced using Collector-C. The rougher concentrate with 20% Cr_2O_3 was refloated, adding 1000 g/t Collector-C at a pH of 9 and a CMC depressant of 100 g/t. The results are depicted in Fig. 11. The Cr_2O_3 grade was upgraded to 25% while the SiO_2 grade dropped to 22.8%. The CMC was efficient in depressing the silicates, which ultimately increased the grade of chromite. Future work includes introducing more cleaning stages and testing other depressants and dosages. The ultimate objective of exceeding 40% Cr_2O_3 grade is still elusive; meanwhile, further investigation involves a multiple-cleaning circuit, inclusion of co-collectors to improve chromite recovery, and testing other depressants and dosages.



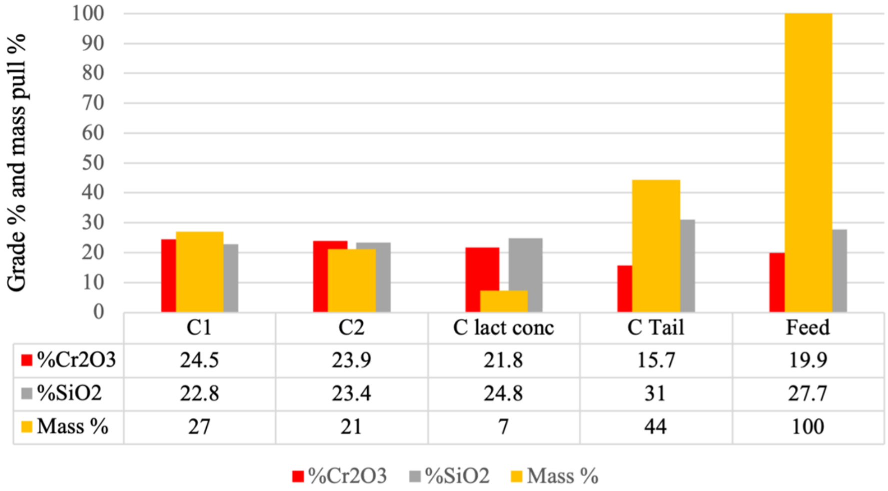
Flotinor-VF2711

	2	4	6
%Cr2O3	20	16	15
%SiO2	26	31	33
% Mass pull	14	20	23

Collector-C

	2	4	6
%Cr2O3	20	18	17
%SiO2	25	30	29
% Mass pull	23	16	13

Fig. 10. Flotinor-VF2711 and Collector-C product's Cr_2O_3 grade %, SiO_2 grade % and mass pull % as a function of flotation time at 1000 g/t and a pH of 9



	C1	C2	C lact conc	C Tail	Feed
%Cr2O3	24.5	23.9	21.8	15.7	19.9
%SiO2	22.8	23.4	24.8	31	27.7
Mass %	27	21	7	44	100

Fig. 11. Collector-C product's analysis and mass pull % as a function of flotation time at 1000 g/t and a pH of 9

4.3. The floatability of a -25 µm tailings sample

The -25 µm UG2 flotation tailings sample was floated at a pH of 9, using Flotinor-VF2711 and Collector-C at a constant dosage of 1000 g/t. The resulting Cr_2O_3 grade, SiO_2 grade and the mass pull % are depicted in Fig. 12. Conc 1, Conc 2 and Conc 3 were collected after two minutes, four minutes and the residual concentrate, respectively. The -25 µm fraction did not respond to the surfactants under the optimal conditions for the +25 µm sample. The collective mass pull % did not exceed 30% for both collectors.

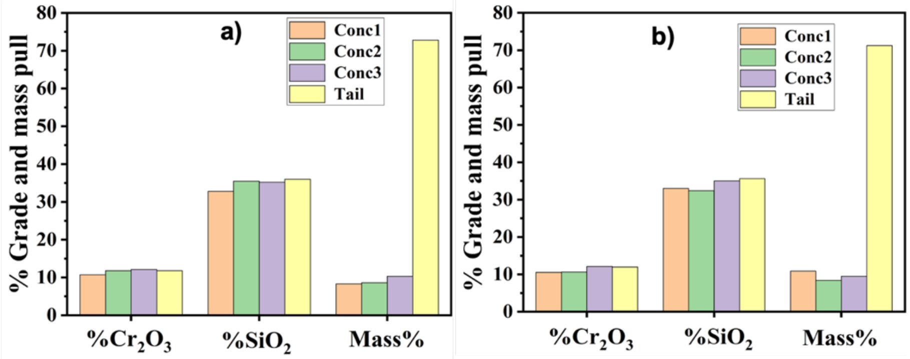


Fig. 12. Floatability of a -25 µm UG2 flotation tailings using a) Flotinor-VF2711 and b) Collector-C

5. Discussion

It is intriguing that collectors have a unique interaction with different particle size fractions, as displayed in Fig. 5. The effect of particle size on chromite floatability seems to be sensitive to the type of collector used. de Medeiros and Baltar (2018) reported on the effect of particle size on particle floatability. The collector type, specifically the collector's carbon-chain length, had a predominant effect on the mechanism of particle-bubble attachment. The long-carbon-chain collectors were efficient in attaching the finer particles, whereas the shorter-chain collectors mostly collected the coarser particles (de Medeiros and Baltar, 2018; Cook and Gibson, 2023). For shorter-carbon-chain collectors, physical adsorption is a dominant mechanism of particle-bubble attachment. Floatability is a function of particle size, where coarser particles (<75/>14 µm) are preferentially floated rather than finer particles (<14 µm). With longer-chain collectors, chemical adsorption is a predominant adhesion mechanism; as such, particle size has a minor effect on the floatability (de Medeiros and Baltar, 2018).

de Medeiros and Baltar (2018) tested dodecylamine, an amine-based collector with shorter carbon chains, and sodium oleate-oleic acid, a fatty acid with longer carbon chains. Dodecylamine preferentially floated the coarser particles but struggled with the finer particles. With the fatty acid, both the fines and the coarse particles were floated (de Medeiros and Baltar, 2018).

Collector-C is a fatty acid with an 18-carbon chain; it comprises oleic, ricinoleic and linoleic acids. For Collector-C, all the concentrates were finer than the feed; however, the first concentrate was the finest. The finer particles were the fast floaters. After the first two minutes, the concentrate became coarser. On the contrary, with Flotinor-VF2711, the finer particles were the last to float, and the two-minute concentrate was coarser than the feed, whereas the last concentrate (residual suspension) had the finest particles. Flotinor-VF2711 is an amine-based anionic collector; amines have shorter-carbon chains varying from 8 to 18, compared to oleic and linoleic acids that have 18 carbons [20]. Based on de Medeiros and Baltar's (2018) work, it is plausible that the two collectors demonstrated preferential flotation of particles as a function of particle size due to their carbon chain length.

5.1. The effect of pH and collector dosage on chromite recovery

The speciation of fatty acids as a function of pH and collector concentration is discussed by Cook and Gibson (2023). A fatty acid like oleic acid has five speciations, i.e., aqueous, liquid, oleate dimer, anion and acid-anion complexes. Aqueous and liquid forms are stable below pH 8.6, while dimer, ionic and acid-anion complexes are stable above pH 8.6. The five species coexist at maximum concentrations around pH 8.6, which is during the transition from aqueous/liquid to anion/acid-anion complex (de Medeiros and Baltar, 2018; Cook and Gibson, 2023). As the concentration of the fatty acid changes, the transitioning pH of the speciation changes; at low concentrations, the shift occurs at high pH, while at high concentrations, it is at low pH (Cook and Gibson, 2023). With varied concentrations of the fatty acid in solution, the pH at which all species of fatty acids are at maximum may shift from 8.6 to either a higher or a lower pH.

Since Collector-C comprises oleic, ricinoleic and linoleic acids, the fatty acid speciation as a function of pH can be a plausible mechanism for the high Cr_2O_3 grade observed between pH 8.5 and pH 9. The presence of the acid-ion complex around pH 9 is believed to have enhanced the floatability of chromite (Cook and Gibson, 2023).

The change in fatty acid speciation can also affect the mechanisms of collector adsorption onto the particle since the different species carry different ionic charges. The chromite species can undergo dissolution and hydrolysis at alkaline pHs. The chromite's cationic species (Fe^{2+} and Mg^{2+}) produce OH^-, OH^{2+} or neutral complexes as the pH increases. OH^- enhances chromite flotation while OH^{2+} depresses flotation. The cationic complexes reverse the particle's charge to positive. This alters the collector's adsorption mechanism on the surface (Güney et al., 1999; Yiğit et al., 2014; Budemberg et al., 2019). The nature of adsorption is electrostatic when a charged collector adsorbs onto an oppositely charged site on a particle, whereas chemical adsorption is when the chromite surface is covered by a monolayer of the surfactant [18], [20]. Under alkaline conditions, chemisorption is a likely mechanism where stable compounds interact with cations. The adsorption mechanism also influences bubble-particle attachment, further complicating the floatability of chromite particles as a function of pH (de Medeiros and Baltar, 2018). Chromite is a complex compound that can interfere with ions such as Al^{3+}, Fe^{3+} and

Mg^{2+}. The anionic/fatty acid collectors primarily interact with the surfaces of oppositely charged particles or cationic sites on mineral surfaces (Feng and Aldrich, 2004; Cook and Gibson, 2023). The presence of Al^{3+}, Fe^{3+} and Mg^{2+} on the chromite structure might serve as a conducive site for particle-collector interactions at higher pHs (Guven et al., 2020). The dissolution of cationic sites on chromite surfaces interferes with the chromite's point of zero charge, which then affects the pH at which the chromite can be selectively floated. Without a collector, the chromite's point of zero charge is at pH 4; below pH 4, chromite is positively charged, while above this pH, it is negatively charged. Collectors attract an oppositely charged particle. Therefore, the efficiency of a collector does not solely depend on the collectors' properties; floatability is also affected by the properties of the particle of interest (Yiğit et al., 2014; Guven et al., 2020). From pH 8.5 to pH 10, it is envisaged that the adsorption mechanism of a collector on a chromite's surface would vary depending on the collector's active speciation as well as the chromite's dominant charge. This explains why the Cr_2O_3 grade drops as the pH increases above pH 9.

The two-minute flotation time at pH 9 and 1000 g/t yielded the highest Cr_2O_3 grade of 19.9% and the lowest SiO_2 grade of 27.4% (Fig. 10). Increasing the flotation time beyond two minutes favoured the SiO_2 grade, which signified that chromite is fast floating. The effect of particle size could significantly affect the sensitivity of chromite to flotation time. According to de Medeiros and Baltar (2018), after 60 seconds, the coarse particles reach optimal floatability, while the fine particles supersede the coarse particle floatability after 60 seconds. As seen in Figs. 5 and 6, the particle size plays a significant role in chromite floatability. With an amine-based collector, fine particles floated last, and coarse particles were fast floaters. With a fatty acid collector (longer-carbon chains), the finer particles floated first, leaving a coarser tailing. There is a potential synergism between the flotation time, the particle size and the collector type, which could affect chromite's response to flotation.

5.2. The efficacy of four collectors

For all collectors except Lupromin-476, the highest Cr_2O_3 grade was in the first two minutes. From four minutes to the last concentrate, the Cr_2O_3 grade decreased; when Lupromin-476 was used, the Cr_2O_3 grade increased slightly from 15 to 16% in the last concentrate. This was accompanied by the lowest mass pull %; it is plausible that the slight increase in Cr_2O_3 grade was due to the concentration effect since most of the ore had floated. This observation will be investigated further in ongoing research.

Collector-C gave the best results with the Cr_2O_3 grade dropping from 20% (after two minutes) to 17% at the last concentrate. The grind of all the concentrates was finer than the feed. The SiO_2 was the lowest in the two-minute concentrate, and just slightly higher in the last concentrate. Collector-C seemed to preferentially float the finer particles, seeing that the concentrate grind was always finer than the feed. This highlights the potential effect that the carbon chain length of the collector has on floatability, especially for varied particle sizes. The single-stage cleaning of the rougher concentrate improved the Cr_2O_3 grade to 25%. It is envisaged that with a multiple cleaning circuit, higher Cr_2O_3 grades can be achieved.

Flotinor-VF2711 had the second-best Cr_2O_3 grade of 20% in the first two minutes, after which the grade dropped sharply to below 15% in the last concentrate (Fig. 10). On the contrary, the SiO_2 grade was the lowest in the two-minute concentrate, but it was the highest in the last concentrate. This correlates with the concentrate grind (Fig. 4), in which the first concentrate was coarser, the second concentrate was slightly finer, and the last concentrate was the finest. With the high content of SiO_2 and the fineness of the last concentrate, it is plausible that the flotation with Flotinor-VF2711 was more of a physical phenomenon than chemical adsorption.

Lupromin-476 and Betacol-175 yielded the lowest Cr_2O_3 grades; this could largely be attributed to the lack of selectivity of these collectors. A high amount of SiO_2 was detected in the concentrate. Since Betacol-175 is an anionic collector, it could be more efficient in the acid conditions where the chromite charge is positive.

5.3. The floatability of a -25 μm tailings sample

Theoretically, flotation is efficient at particle sizes >20 μm, while the finer fraction is difficult to float (Farrokhpay et al., 2020). Pease et al. (2006) argue that the fine fraction is floatable; however, this fraction needs to be optimised separately from the coarser fraction since the conditions optimal for the coarse fraction are not suited for the finer fraction. The latter part of this project aimed to determine whether the -25 µm fraction could be floatable to recover the chromite. About 60% of the UG2 tailings sample consists of ultra-fine material (-25 µm), thus it is essential to devise a method to effectively recover chromite from the -25 µm fraction. For fine particles, low density and high surface area are some of the factors that impair the collision and adhesion of fine particles to the bubbles; the high surface area results in low collector adsorption density [20]. Farrokhpay et al. (2020) argue that using micro-bubbles enhances the floatability of ultra-fines owing to the high attachment efficiency of small particles to microbubbles. The introduction of microbubbles and reverse flotation is strongly recommended for the ultra-fines, seeing that the Cr_2O_3 grade could not be improved using direct flotation. Another method of interest is elutriation. These methods are currently being investigated in the subsequent phase of this project.

6. Conclusions

A UG2 flotation tailings sample has a magnesia-rich chromite and the silicates of iron and calcium. The chromite has a positive zeta potential below pH 5, after which the zeta potential is negative from pH 6 to pH 11. The associated gangue, silicates, have a positive zeta potential only at pH less than 2. The MLA analysis confirmed that the particles are not fully liberated even at the optimal flotation PSD, which is >74/>10 µm; however, SEM-BSE and X-ray mapping did not detect any significantly locked particles.

Although direct flotation is a promising method for upgrading low-grade chromite tailings (12% Cr_2O_3) to a market grade of >40% Cr_2O_3, the direct flotation conditions must be optimised. The highest Cr_2O_3 grade of 25% was achieved after one cleaning cycle using Collector- C in the presence of a CMC depressant. Without a depressant, the highest grade reached was 20% Cr_2O_3 and 24.8% SiO_2.

A pH between 8.5 and 9 was optimal for Cr_2O_3; increasing the pH to 10 enhanced the SiO_2 grade at the expense of the Cr_2O_3 grade. A collector dosage of 1000 g/t yielded the highest Cr_2O_3 grade; however, at 800 g/t, the chromite minima was observed. This could be attributed to variations in the collector-particle attachment mechanism as a function of collector concentration. The flotation time of two minutes yielded the highest Cr_2O_3 grade, while floating beyond two minutes adversely affected the Cr_2O_3 grade.

Varying the collector types depicted high sensitivity to the particle size of the concentrate; this could be related to the collector's carbon-chain length. The interaction between particle size and collector type depended on flotation time. The kinetics of flotation seem to be sensitive to the collector type and particle size. Flotinor-VF2711 preferentially floated the coarser particles first, while the finer particles floated last. On the contrary, Collector-C initially floated the finest particles, after which the coarser particles were observed in the concentrate.

Flotinor-VF2711 and Collector-C were the best-performing collectors based on the highest Cr_2O_3 grade achieved and the associated SiO_2 grade. The -25 µm fraction could not be upgraded using a direct flotation, which could be due to the fineness of the sample, where the effect of the surfactants is potentially weaker than the gravitational and drag forces acting on a fine particle immersed in a fluid. Reverse flotation, elutriation, and flocculation are alternative methods being probed to recover chromite from the ultra-fine particles.

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Supplementary information

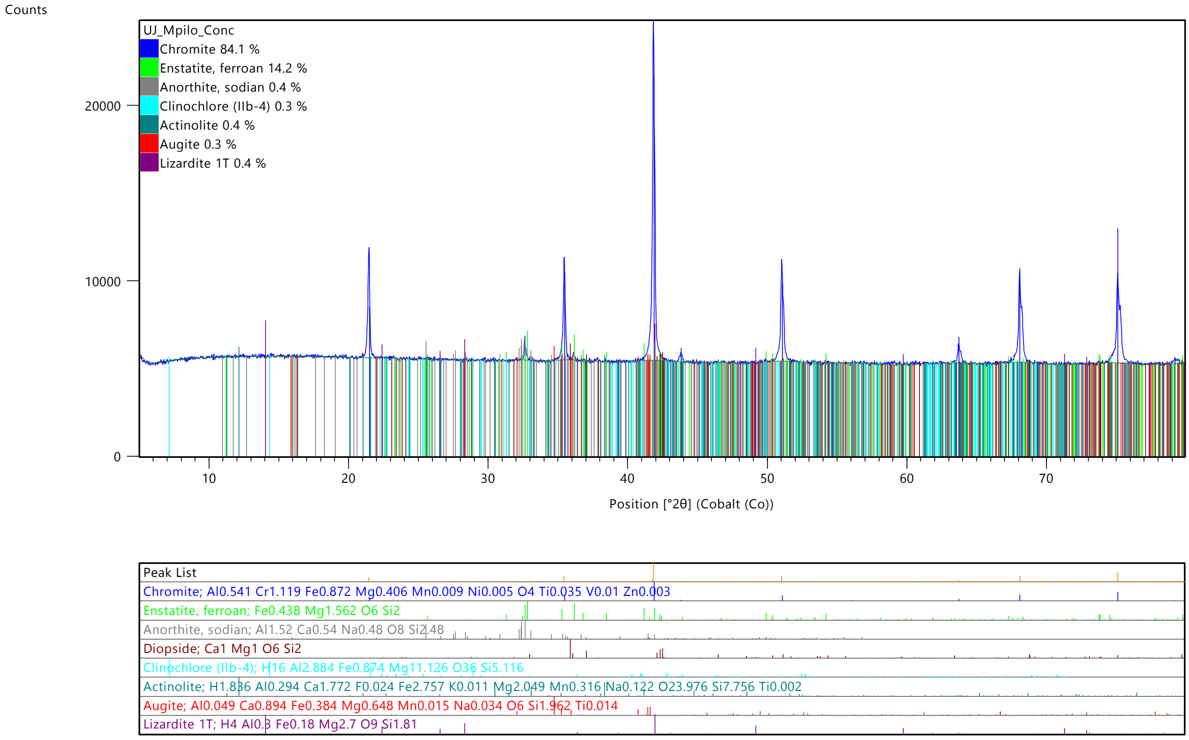

Fig. A1. The XRD analysis of the shaking table concentrate of the +53/-75 µm fraction

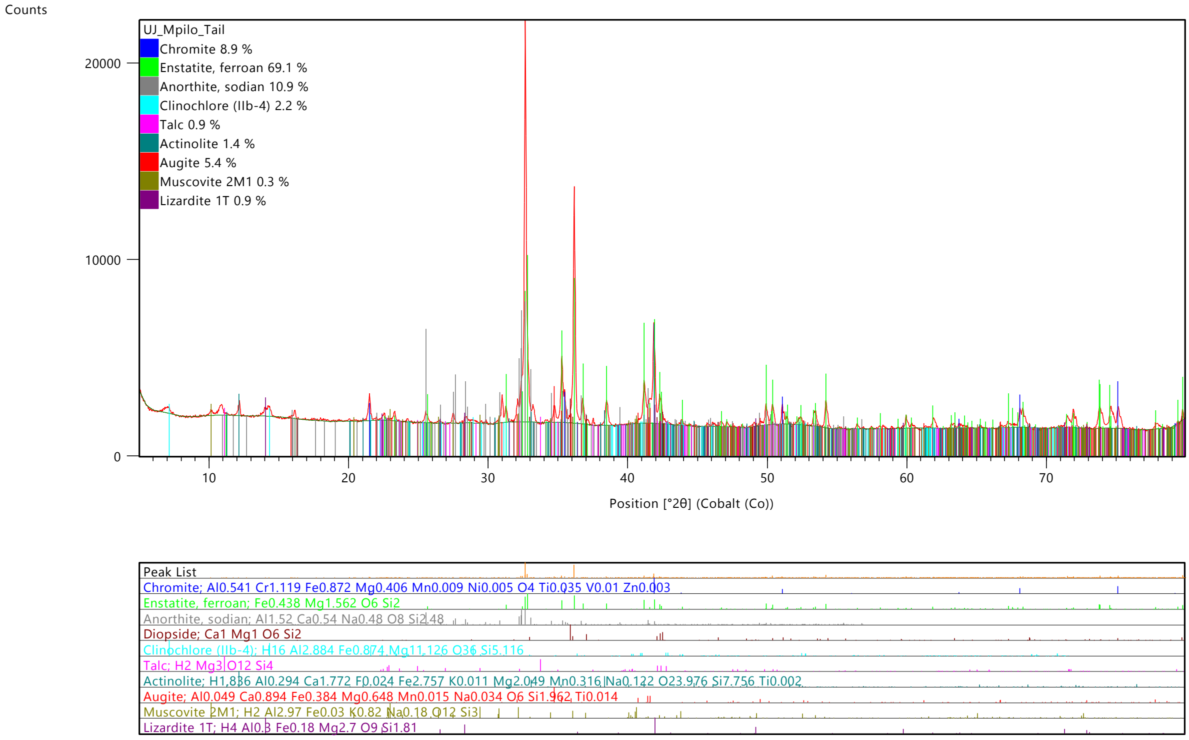

Fig. A2. The XRD analysis of the shaking table tailings of the +53/-75 µm fraction