GOSPODARKA SUROWCAMI MINERALNYMI – MINERAL RESOURCES MANAGEMENT

2022 Volume 38 Issue 4 Pages 205–230

DOI: 10.24425/gsm.2022.143624



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Selective flocculation and recovery of chrome from plant slimes using starch and sodium oleate as flocculants

Introduction

The current challenge associated with beneficiation of mineralogically complex and highly disseminated low-grade ores makes it necessary to fine grind the ores to release the values before recovery. Fine grinding leads to the excessive generation of slime (Yu et al. 2017) and in the South African chrome industry, it is estimated that about 25% of the mineral value of chrome is lost to ultrafine tailings/slime during processing (Da Corte et al. 2019). The source of chrome ore in South Africa is the Bush-veld Igneous Complex (BIC), a large

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geological intrusive body that is divided into eastern, western and northern lobes and hosts chromite deposits that occur as strati-form layers of massive chromitite. The layers of significance are all present in a lower portion of the BIC known as the critical zone. Chrome layers are grouped together in three groups. The lower group (LG) consists of seven chromitite layers, the middle group (MG) consists of four main chromitite layers and the upper group (UG) consists of two chromitite layers. The average chrome content and the Cr/Fe ratio of the individual layers decrease upwards from LGs to the UGs while the platinum group metals (PGMs) content increases in the same direction. Traditionally, the LG and MG layers have been exploited for chrome production while the UG has been exploited for PGMs. The chromite seam of the middle group (MG) contains intermediate concentrations for both chrome and PGE mineralization but also displays a general decrease in grain size from the lowermost layers towards the uppermost layers. As a result of the finer grain size and low chrome content (18–25% Cr₂O₃), the MG layers require finer milling to adequately release the chrome grains and this inadvertently leads to slime generation. However, the UGs, which are a source of PGMs, are generally finely milled to release the PGM grains, the fine milling produces fine chrome which is recovered as a by-product. Therefore, the exploitation of MG and UG resources for chrome recovery is accompanied by the production of ultrafine particles or slimes that are rich in chrome.

The addition of value associated with the processing of slimes generated from mining and mineral processing operations has started to attract a lot of research interest (Tankosić and Sredić 2021). Slime dams have become a secondary source of chrome and presents a huge economic opportunity to make the chrome industry more sustainable (Beklioglu and Arol 2004). Slimes generally consist of particles that are less than 50 µm (skewing to < 20 µm) in size, and these particles are generated during the mining processes (primary slimes) and during comminution stages (secondary slimes) (Beklioglu and Arol 2004). The ultrafine particles when treated along with coarser particles in conventional chrome concentration processes such as gravity separation, dense medium separation (DMS), magnetic separation and flotation, respond poorly and introduce inefficiencies in these conventional separators (Panda et al. 2010). In gravity concentrators like spirals and jigs, fine particles are undesirable because they do not settle fast enough (Beklioglu and Arol 2004). In DMS separators, fine particles tend to alter the medium density as they remain suspended in the liquid for too long and the change in the medium density and viscosity reduces the sharpness of separation between sinks and floats (Da Corte et al. 2019). In flotation, gangue fines generally contaminate the concentrate by entrainment and entrapment. This lowers the concentrate grades. Gangue fines are also notorious for coating mineral particles (slime coating), deactivating the value minerals and making their attachment to bubbles difficult (Hart et al. 2018). Slimes are therefore normally excluded in separation processes by de-sliming the slurry to improve the performance of concentration processes. The slimes end up in slimes dams as waste (Panda et al. 2013). Figure 1 presents a simplified process flow diagram for a chromite beneficiation process showing a de-sliming cyclone removing slimes before concentration happens.

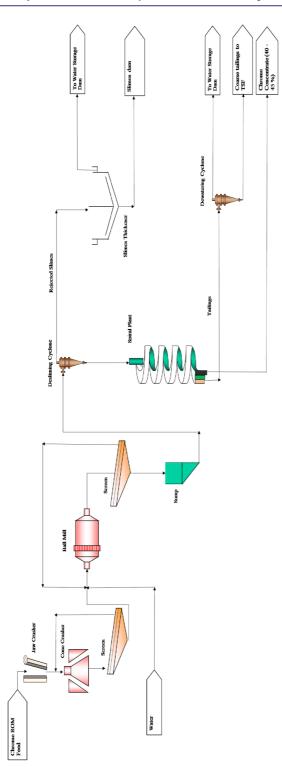


Fig. 1. Simplified process flow diagram for a chromite beneficiation process

Rys. 1. Uproszczony schemat przepływu procesu wzbogacania chromitu

Developing an effective process for the recovery of chrome values from slimes will have a positive impact on the chrome industry. Chrome-processing plants will have an opportunity to re-mine and process historic slime dams previously discarded as waste, thus saving the scarce natural resources. Chrome yields/ton of feed material processed on an ongoing basis will increase when arising slimes are simultaneously processed without first disposing of them. Environmental sustainability will also improve by reducing the waste footprint and increasing the usability of final waste by making it more benign through the removal of more heavy metals (Çicek et al. 1998; Dogan et al. 1998; Guney and Önal 2000; Panda et al. 2015; Tripathy et al. 2019).

Several techniques have been considered to treat slimes. Existing technologies for chrome concentration like spirals, shaking tables, magnets and flotation have been re-purposed to process chrome slimes with varied success (Cicek et al. 1998; Dogan et al. 1998; Güney and Önal 2000; Murthy and Tripathy 2020). In spirals, which consists of an open trough that twists downward in a helix configuration around a central axis, separation is achieved through a combination of forces that act on particles as they move down the trough of the spiral. These forces include gravitational forces, centrifugal force, hydrodynamic drag, lift and friction forces. Materials are separated through stratification caused by centrifugal forces and differential settling and this causes the migration of heavy particles through the bed and into the inner part of the conduit and the lower-density particles are carried with the bulk of the water to the outside of the spiral as the slurry makes its way down the spiral. The main process variables of a typical spiral concentrator are the feed flow rate, the feed pulp density and the splitter position. The optimum feed particle size for the effective separation in spirals has been found to be between 2 mm and 75 µm. Mokoena and Nheta (Mokoena and Nheta 2020) did an analysis of spiral chrome tailings from one South African chrome plant and found that tailings with an average grade of 20% Cr₂O₃ had a finer fraction of below 75 microns constituting 22% by mass with a grade 33% Cr₂O₃. Tripathy et al. (Tripathy et al. 2010) also did some studies to concentrate an ultrafine chromite ore using spirals, the ore was 70% passing 75 microns in particle size with a chrome grade of 21% Cr₂O₃. In this work, it was possible to achieve a good concentrate grade of 48.54% Cr₂O₃ albeit at very low recoveries of 22%. It was observed that most of the ultrafine chrome was lost with the water reporting to the tailings stream. Recovery was also found to be inversely proportional to pulp density, with a low pulp density of about 10% recording the highest recovery. This indicates that conventional spirals do not optimally recover ultrafine chromite mineral particles.

Shaking tables have been used for treating ultrafine chrome with better results. A shaking table is an inclined rectangular deck fitted with small, tapered stripes called riffles to obtain a turbulent flow of water. Mineral components are stratified by superimposing a lateral oscillating force on the flowing film. The flowing water film helps the lighter particles (gangue) to move from one riffle to the other, whereas the oscillating force moves heavier particles (minerals) along the direction of the riffles. In shaking table separation, the important variables in the separation are the angle of the table deck, the length of the stroke, the frequency of the stroke, the splitter position, the feed rate, the pulp density, the wash water

and the riffle height. Seifelnasr et al. (Seifelnasr et al. 2012) studied the separation of chrome ore of grade 30-35% Cr₂O₃ on the shaking table. Seifelnasr et al. (2012) found that treating a close feed size range is better than a wider size range. This is because when the size range is closer, the density difference becomes more dominant in effecting the separation.

Another technology that has been used for chrome processing is magnetic separation. However, there is limited work that has been reported concerning the application of magnetic separation to ultra-fine chromite (Tripathy et al. 2019). The attraction of magnetic separation is that when the density of slurry is reasonably controlled, the effect of particle size on separation is very low. Altin et al. (Altin et al. 2016) studied the beneficiation of very low-grade ultrafine chrome tailings with 2.60-5% Cr₂O₃ through vertical ring pulsating high gradient wet magnetic separator (VPHGMS) and found that the magnetic process could only produce a concentrate of 6-12% Cr₂O₃ grade at 55-80% recovery. This concentrate was subsequently upgraded on a shaking table to a concentrate of 41-50% Cr₂O₃ with a recovery level of 29-43%. This work suggested that at fine to ultrafine particle size and low feed grade, magnetic separation alone is not capable of producing a saleable grade of chrome concentrate. In the work of Tripathy et al. (Tripathy et al. 2019), magnetic separation and the mineralogical characterization of chromite fines to enhance the Cr:Fe ratio was investigated. A rare earth drum magnetic separator, a rare earth roll magnetic separator, an induced roll magnetic separator, and a wet high-intensity magnetic separator were used and the results were compared. The fine chromite was upgraded from a feed material with a Cr:Fe ratio of 1.6 to a concentrate Cr:Fe ratio of 2.2 at a yield of 55.7% through the use of an induced roll magnetic separator, which performed significantly better than the other magnetic separators. Sometimes, magnetic separation can be difficult, especially where there are components in the gangue that are also paramagnetic, like chromite.

The separation of fine chromite from the gangue material is very difficult outside the range of gravity separation and magnetic separation conditions. Sometimes, the particles are so fine that the particles of chromite and gangue especially serpentine behave in a similar way under hydrodynamic conditions. The work of Gallios et al. (Gallios et al. 2007) involved the separation of chromite from serpentine gangue and observed that serpentine, a hydrated magnesium silicate, has similar surface properties to chromite. In such a case, separation flotation can be adopted. Flotation is a physico-chemical separation method used to separate and concentrate ores by altering mineral surfaces to a hydrophobic or hydrophilic condition. The surfaces are then either repelled or attracted by water. Those mineral surfaces that are rendered hydrophobic then attach to bubbles and float. The flotation technique is more versatile as it can be manipulated by using modifying agents so that the minerals behave differently in the presence of collectors. Gallios et al. (2007) were able to identify a reagent suite and conditions that promote the separation of ultrafine chromite from serpentine gangue. They found that chromite floats well at medium concentrations of sodium oleate of 20–30 mg/l in the alkaline pH range. In their work, they also found that carboxymethyl cellulose strongly depresses chromite at the alkaline pH region while fluorosilic acid, cyclodextrin and ethylene diamine-tetra acetic acid (EDTA) activates flotation at acidic and neutral pH values.

One of the promising techniques that has been widely tried in the recovery of iron ore ultra-fines on both experimental and commercial scales with promising results is selective flocculation (Sworska et al. 2000; Panda et al. 2010). This is a process in which fine mineral particles suspended in a liquid are preferentially agglomerated by the addition of a selective flocculent while the gangue material remains suspended. Selective flocculation exploits the surface characteristics of different minerals in the ore (Da Corte et al. 2019). According to Mathur et al. (Mathur et al. 1999) and Panda et al. (Panda et al. 2010) it occurs in the following four stages: dispersion of particles, selective adsorption of the organic flocculent on the surface of the desired mineral to be flocculated, while the unwanted minerals (gangue) remain suspended in the solution, formation of flocs through conditioning at low shear and solid-liquid separation where the flocculated minerals are separated from the dispersed gangue particles (Tankosić and Sredić 2021). Due to the low shear required to grow the flocs and the separation of flocculated mineral phase from gangue by gravity, selective flocculation is considered a less energy-intensive and more cost-effective option for recovering minerals from slimes. A successful separation by selective flocculation therefore depends on how well the minerals are liberated, the extent of dispersion of the particles from each other and on the selectivity of adsorption of the flocculants on the particles of interest (Cicek et al. 1998; Dogan et al. 1998; Guney and Önal 2000; Panda et al. 2015). The degree of the dispersion of particles from each other strongly depends on the Zeta potential, a property in mineral processing that can be manipulated to improve separation when particles are fine and cannot respond positively to the gravitational laws. The zeta potential determines the possibility of particles to coagulate or to be stable in suspension. Coagulation is reported when particles have a zeta potential value in the zone between -30 mV and +30 mV, at a potential beyond this range, the electrostatic repulsion between particles is typically strong enough to prevent the attraction of particles and results in stable dispersions (Marsalek 2012; Tankosić and Sredić 2021). Effective separation is therefore enhanced by using a correct dispersant that can keep the gangue minerals dispersed but not aggressive enough to re-disperse the flocculated mass of valued minerals in the suspension (Panda et al. 2015).

There is limited literature on the selective flocculation of chrome ultra fines, a handful of available articles focus on synthetic ores (Tripathy et al. 2019; Panda et al. 2015). Panda et al. (2015) studied the effect of the main process variables on the selective flocculation of synthetic chrome slime mixtures and found that the process is influenced to a large extent by the degree of dispersion, pH and the dosage of flocculent.

The purpose of the study is to determine the feasibility of selectively flocculating chrome from actual plant chrome slimes by investigating the effect of flocculent and dispersant dosages at a constant pulp density and pH. The study also evaluated the achievable grades and recoveries of chrome in the flocculated mass during selective flocculation. The flocculants used were sodium oleate and raw corn starch and sodium silicate was used as the dispersant.

1. Materials and methods

In this section, the materials and reagents used in the investigation and the experimental setup and methods are discussed.

1.1. Materials

1.1.1. Chrome ore slime

The chrome ore slime sample was obtained from a chrome processing plant in the North-West province of South Africa. A de-sliming cyclone overflow stream was sampled at hourly intervals over a twelve-hour period to obtain a representative bulk sample of the slimes. The composite bulk sample was mixed, dewatered, dried and weighed. It was split using a riffle splitter into 1000 g representative aliquots which were used for analysis and experiments.

A 1000 g portion of the sample was used for head assay analysis to give the chemical composition of the feed material. This was done by pulverizing the sample and analyzing it using X-ray fluorescence spectroscopy (XRF), as in Tripathy et al. (Tripathy et al. 2019). The other portion of the sample was also pulverized and analyzed using an X-ray diffractometer to determine the mineral phases present as well as their relative abundances. Particle size distribution (PSD) analysis of the slimes was done by screening the sample through 75, 53 and 25 μ m screens.

1.1.2. Chemical reagents used

The flocculants used were corn starch $(C_6H_{10}O_5)_n$ and analytical grade sodium oleate $(C_{18}H_{33}NaO_2)$. Sodium silicate (Na_2SiO_3) was used as the dispersant and sodium hydroxide (NaOH) as a pH modifier. These reagents were supplied by Laboratory Suppliers (South Africa).

Raw corn starch was selected as one of the flocculants because of its proven affinity for FeO and Fe₂O₃ as demonstrated in the studies of iron ore fines flocculation (Panda et al. 2010, 2011, 2013). Chromite mineral spinels have been found to inherently contain FeO and Fe₂O₃. Chrome (Cr₂O₃) itself has a similar molecular structure to Fe₂O₃, which suggests that starch could potentially work as a flocculent for chrome slimes. Sodium oleate, which is a good flotation collector for chromite, has also been found to be effective in flocculating iron-bearing minerals (Pascoe and Doherty 1997) this is why it has been considered in this work as a flocculent for chromite.

Sodium silicate was selected on the basis of being a good dispersant for silicate-based minerals, which make up the bulk of the gangue minerals in the chrome slimes under investigation. The other attraction of corn starch, sodium oleate and sodium silicate is that they are relatively inexpensive reagents (Hart et al. 2018).

Corn Starch

Corn starch solution was prepared by dissolving corn starch pellets in water at a temperature of 120°C (thermal gelatinization) and adjusting pH to 11. The solution was stirred for thirty minutes and subsequently allowed to cool down to room temperature before use. The starch solution was freshly prepared daily to avoid degradation, and it was stored as a 1 mg/ml concentration solution.

Sodium Oleate

Sodium oleate flocculent was prepared using a method recommended by Pascoe and Doherty (Pascoe and Doherty 1997). This method involved heating water to 60°C on a hot plate and adjusting pH to 11, before adding sodium oleate and stirring. Once sodium oleate had dissolved, the solution was allowed to cool down to room temperature before use. The sodium oleate solution was prepared and stored as 1 mg/ml concentration solutions.

Sodium Silicate

Analytical grade sodium silicate pellets were dissolved in distilled water to produce the appropriate dosages of dispersant solutions.

pH Modifier

Analytical grade sodium hydroxide pellets were used to prepare a solution used as a pH modifier.

1.2. Experimental set-up

Figure 2 shows the sequence of the selective flocculation experimental test-work runs.

Figure 3 shows the experimental set up that was used for the preparation of the slurry and the conducting of settling tests. The slurry was prepared in a 1000 ml beaker and kept in suspension using a magnetic stirrer operating at a low frequency (low shear). A pH meter was used to measure and monitor the pH of the slurry. After conditioning with a dispersant, flocculent and pH modifier, the slurry was transferred from the preparation beaker into the measuring cylinder for settling. The cylinder was closed with a rubber stopper and gently inverted five times to create a homogenously mixed suspension before the slurry was allowed to freely settle for two minutes.

Table 1 shows the experimental conditions of the test-work. The solids concentration of the slurry was kept constant at 15% solids by weight to mimic the industrial conditions of the solids concentration of the slimes stream as it exits the de-sliming cyclone. The pH was fixed at 11 to support the dispersion of gangue minerals, it has been shown that the zeta potential of clay and silicate minerals varied between –30 and –60 mV in alkaline solutions of pH around 10–11. Beklioglu and Arol (Beklioglu and Arol 2004) also showed that starch with

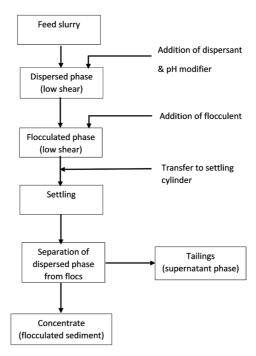


Fig. 2. The selective flocculation test-work sequence

Rys. 2. Sekwencja testów selektywnej flokulacji



Fig. 3. Slurry preparation setup and settling test setup

Rys. 3. Konfiguracja przygotowania szlamu i konfiguracja testu osadzania

Table 1. Experimental conditions

Tabela 1. Warunki doświadczalne

Dispersant	Diamonant	Flocculant	Flocculant		
Sodium silicate	Dispersant condition time	Corn starch/ Sodium oleate	conditioning time	Slurry	рН
g/ton _{slurry}	mins	g/ton _{slurry}	mins	% Solids	
44		18			
88		18			
106		18			
133		18			
44		44			
88	2	44		1.5	11
106	3	44	2	15	11
133		44			
44		62			
88		62			
106		62			
133		62			

a pH of around 11 does not adsorb to minerals like serpentine and feldspar but adsorbs very well to chromite.

The dispersants and flocculants were varied at three levels. On the completion of each settling test, the dispersed supernatant was siphoned off and the settled solids were removed, dried, weighed and analyzed.

In order to investigate whether the settling test was reproducible, the above-mentioned test process was repeated three times.

1.3. Zeta potential

The zeta potential was not monitored in the experiment since the tests were conducted at a single pH value of 11. The zeta potential plays a vital role in determining the dispersion tendency of particles in a specific aqueous solution. It determines the possibility of particles to flocculate or to be stable in suspension. At a pH of 11, the zeta potential of clay minerals is in the range of between –30 and –60 mV, which supports a well dispersed and stable supernatant (Jeldres et al. 2019; Xu et al. 2003; Zhao 2017). Beklioglu and Arol (Beklioglu and

Arol 2004) also showed that starch with a pH of around 11 does not adsorb to minerals like serpentine and feldspar but adsorbs very well to chromite.

1.4. Particle size distribution

Figure 4 is the graph of the slimes feed material PSD expressed as cumulative % passing on the different screen sizes of 75, 53 and 25 μ m.

Figure 4 shows that 80% of the particles were below 53 μ m which qualifies the feed material as ultra fines.

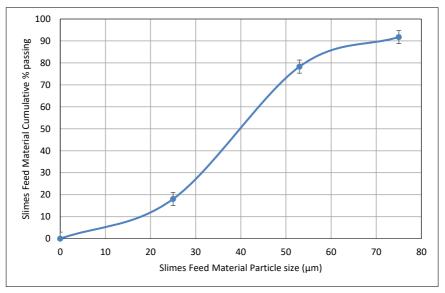


Fig. 4. Particle size distribution of the slimes stream material

Rys. 4. Rozkład wielkości cząstek materiału strumienia szlamu

1.5. X-ray fluorescence spectroscopy (XRF)

The head grade chemical assay and experiment samples chemical analysis was performed using XRF. The analyzer is a PANalytical Epsilon 3 XL ED-XRF spectrometer, equipped with a 50 kV Ag-anode X-ray tube, six filters, a helium purge facility and a high-resolution silicon drift detector, and calibrated using a number of international and national-certified reference materials (CRMs).

Table 2 shows the head grade XRF results of the chrome slimes material in terms of chrome content as well as the associated minerals. The head grade of the bulk sample was

Table 2. Chrome ore slimes composition – XRF Analysis

Tabela 2. Skład szlamów rudy chromu – analiza XRF

Component	Composition (wt.%)
Cr ₂ O ₃	22.92
SiO ₂	28.15
Fe ₂ O ₃	18.37
Al ₂ O ₃	14.05
MgO	10.02
CaO	3.86
Na ₂ O	0.64
TiO ₂	0.50
K ₂ O	0.26
MnO	0.24
NiO	0.11
P_2O_5	0.04
Loss on ignition (LOI)	0.84
Total	100.00

measured using three different aliquots and the variability in the content of the main components was insignificant across the analyzed samples. The average of these was recorded as the representative head grade and is reported in Table 2.

The chrome (Cr_2O_3) content of the slime sample was 22.92% and the other predominant components were SiO_2 , Fe_2O_3 , Al_2O_3 and MgO and together these make up 94% of the minerals in the slimes. This means that elimination by flocculation of silica (SiO_2) , alumina (Al_2O_3) and Magnesite (MgO), which are the dominant minerals, would lead to a better chromite grade (Cr_2O_3) and Fe_2O_3 .

1.6. X-Ray Diffraction Analysis (XRD)

The mineralogical composition of the slime sample was determined using a Panalytical X'pert Pro diffractometer employing the Fe filtered Co-K α radiation. The resulting patterns were processed using the HighScore Plus analytical software and the PanICSD database. Table 3 shows the different minerals identified and their relative abundances.

XRD results show that the chromite mineral spinel makes up about 42%. The results also indicate that feldspar, pyroxene and chlorite are the predominant gangue minerals in the

Table 3. Chrome ore slimes composition – XRD Analysis

Tabela 3. Skład szlamów rudy chromu – aXRD

Mineral	Chemical formula	Composition (wt.%)
Chromite	Cr ₂ O ₃ · FeO(Mg,Al)xOy	41.8
Feldspar	(K,Na,Ca)AlxSiyOz	20.5
Pyroxene	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al) ₂ O ₆	12.7
Chlorite	(Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	11.7
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	4.9
Kaolinite	Al ₂ O ₃ · 2SiO ₂ (H ₂ O) ₂	3.9
Mica	K ₂ Al ₄ (Si ₆ Al ₂ O ₂₀)(OH,F) ₄	2.2
Quartz	SiO ₂	1.1
Olivine	(Mg,Fe) ₂ SiO ₄	0.4
Amphibole	(Mg,Fe,Ca)Si ₈ O ₂₂ (OH) ₂	0.3
FeOx/OH	FeOx/OH	0.1
Carbonates	(Ca,Mg,Na)CO ₃	0.1
Others		0.3
Total		100.0

slimes sample followed by talc, kaolinite, mica and quartz, the rest of the gangue minerals are < 1% and are therefore relatively insignificant.

2. Results and discussion

2.1. Effect of flocculent and dispersant dosages on the grade of flocculated mass

The results presented in Figure 5 show the effect of varying the dosage of the dispersant (sodium silicate) and the flocculent (sodium oleate) on the grade or Cr_2O_3 content of the flocculated mass. The results generally show that significant concentration of the slimes feed material happens during selective flocculation. The test sample used had a head grade of 22.92% Cr_2O_3 and after selective flocculation using sodium silicate and sodium oleate, the flocculated mass Cr_2O_3 content was 39.06% min and 42.55% max which is a significant upgrade in terms of the Cr_2O_3 content. The results also show that at a given flocculent dosage, the concentrate grade increases with dispersant dosage from 44 to 88 g/ton_{slurry} and then decreases when the dispersant dosage is increased from 88 to 133 g/ton_{slurry}.

A high dispersant dosage of 106–133 g/ton_{slurry} causes a significant decrease in the Cr₂O₃ grade when the flocculent dosage is low (18 g/ton_{slurry}), suggesting that at high concentration of dispersant, when there is not enough flocculent, the dispersant could be excessive and maybe causing re-dispersion of the flocculated mineral particles leading to a lower grade of the flocculated mass. However, at higher flocculent dosages the decrease in the Cr₂O₃ grade is gradual. Hart et al. (Hart et al. 2018) studied the infrared spectra of sodium silicate and showed that it contains polymeric or condensed silicate species, and that at high concentrations polymerization occurs on the mineral surface which can increase dispersion of the minerals with its accumulation. This may help to explain the decrease in Cr₂O₃ grade observed at high sodium silicate concentrations for low flocculent dosage.

At low dispersant dosages of 44 g/ton_{slurry} (sodium silicate), an increase in the flocculent dosages from 18–62 g/ton_{slurry} sodium oleate reduces the grade of the flocculated mass progressively suggesting that when the dispersion of the gangue is not sufficient increased flocculent strength causes capture of more gangue particles leading to a reduction in the grade of the flocculated mass. Similar observations were made by Da Corte et al. (Da Corte et al. 2019) in their work on selective flocculation of iron from slimes using sodium oleate. It was observed that stronger adsorption of sodium oleate onto the mineral surface at high concentrations resulted in an increase in the entrainment of gangue thereby reducing the separation efficiency/recovery of the Fe₂O₃ and its grade (Da Corte et al. 2019). At higher dispersant dosages the grade response to increase in flocculent dosages is not that direct.

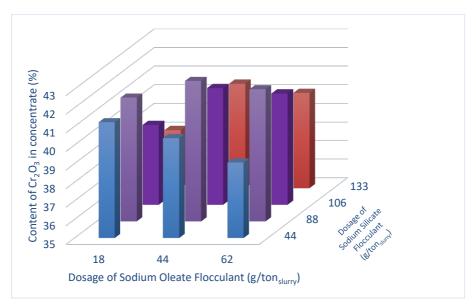


Fig. 5. The effect of sodium oleate and sodium silicate dosage on concentrate grade

Rys. 5. Wpływ dawkowania oleinianu sodu i krzemianu sodu na stopień koncentratu

The maximum Cr₂O₃ grade of the flocculated mass was 42.55%, and it was achieved at sodium silicate dosage of 88 g/ton_{slurry} and sodium oleate dosage of 44 g/ton_{slurry}.

Figure 6 shows the effect of varying the dosage of the flocculent (starch) and the dispersant (sodium silicate) on the grade or Cr₂O₃ content of the flocculated mass. A significant concentration of the feed material was also observed with the use of starch as a flocculent. The affinity of starch and its derivatives to iron bearing minerals has been widely reported before and it is attributed to the complex formation and hydrogen bonding between metal ions on the mineral surfaces and starch molecules (Ravishankar et al. 1995).

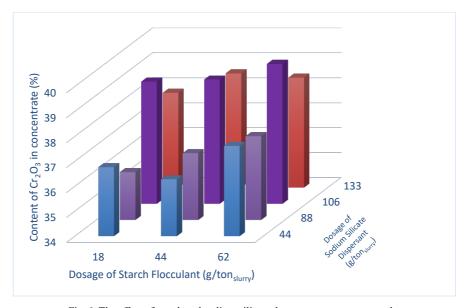


Fig. 6. The effect of starch and sodium silicate dosage on concentrate grade

Rys. 6. Wpływ dawkowania skrobi i krzemianu sodu na stopień koncentratu

The Cr₂O₃ content of the flocculated mass after selective flocculation was 35.92% min and 39.61% max from a feed sample head grade of 22.92%. The results show a general increase in the concentrate grade with increasing starch dosage for all of the tested dispersant dosages. An increase in dispersant dosage is seen to increase the grade up to a dosage of 106 g/ton_{slurry} and a further increase in dispersant concentration to 133 g/ton_{slurry} causes a slight decrease in the grade. The Cr₂O₃ content of flocculated mass was highest at a sodium silicate dosage of 106 g/ton_{slurry} across all the starch dosages. The best grade was recorded at a sodium silicate dosage of 106 g/ton_{slurry} and a starch dosage of 62 g/ton_{slurry}. It is clear that while both flocculants achieved good concentration of the slime sample, sodium oleate performed better than starch in achieving superior grades of concentrate.

2.2. The effect of flocculent and dispersant dosages on chrome recovery to the flocculated mass

Figures 7 and 8 show the chrome recovery to the flocculated mass as a function of the flocculent and dispersant dosages.

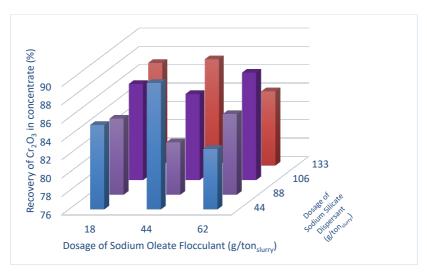


Fig. 7. The effect of sodium oleate and sodium silicate on chrome recovery

Rys. 7. Wpływ oleinianu sodu i krzemianu sodu na odzysk chromu

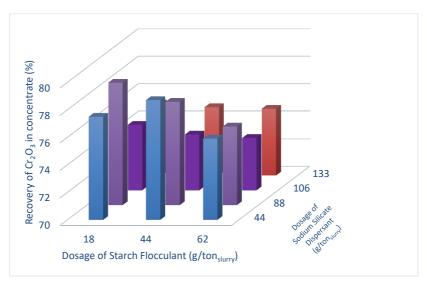


Fig. 8. The effect of starch and sodium silicate on chrome recovery

Rys. 8. Wpływ skrobi i krzemianu sodu na odzysk chromu

The results on the grade and recovery obtained from the different suites of reagents are directly compared in Figure 9. The upper two curves in Figure 9 show the results of the chrome recovery into the floculated mass at different experimental conditions and the two lower curves are the chrome grade curves. The recoveries obtained using sodium oleate floculent were in the range of 80 to 89%, which is significantly higher than recoveries obtained using starch which were in the range of 73 to 79%. The combination of the higher recoveries and superior grades associated with sodium oleate indicates the superior ability that sodium oleate has over starch in terms of binding the chrome minerals.

These results are consistent with observation from Peng et al. (Peng et al. 2020) on flocculation of ilmenite (FeO · TiO₂) ultra fines. Ilmenite has some similarities with chromite in that both minerals have FeO as an integral part of the mineral spinels. In the study, a comparison of flocculation capabilities of soluble starch, sodium oleate, polyacrylamide and carboxymethyl cellulose on the ilmenite ultrafine ore slurry was performed. The results

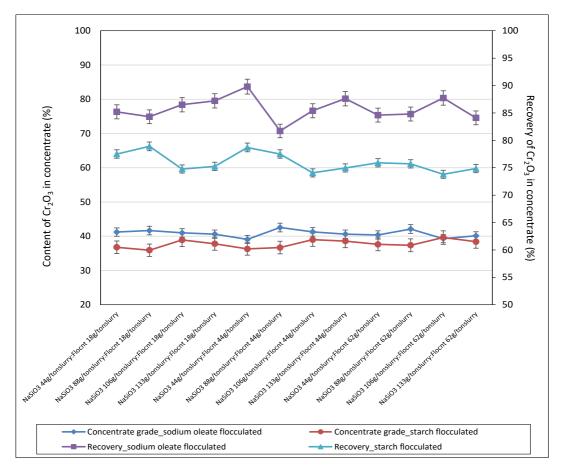


Fig. 9. The effect of dispersant dosage on Cr₂O₃ grade and the recovery of concentrate

Rys. 9. Wpływ dozowania dyspergatora na stopień Cr₂O₃ i odzysk koncentratu

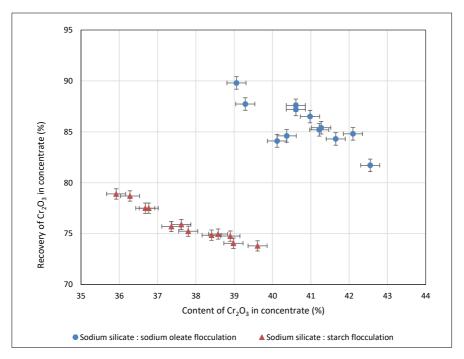


Fig. 10. Chrome recovery – grade curves for selective flocculation

Rys. 10. Odzyskiwanie chromu – krzywe stopni dla selektywnej flokulacji

indicated that different types of flocculants have different degrees with regard to promoting the flocculation of ilmenite. It was found that the addition of sodium oleate quickly formed flocs that settled to the bottom but the effect of adding soluble starch was not so obvious. It was concluded that soluble starch is less suitable for flocculating ultrafine ilmenite particles especially the very fine particles that are less than 23 μ m.

Figure 10 presents the recovery-grade curves for $\rm Cr_2O_3$ in the flocculated mass from the flocculation of the slimes with both sodium oleate + sodium silicate and starch + sodium silicate. The curves show a typical inverse relationship between recovery and grade (Hart et al. 2018; Tripathy et al. 2019). It is evident that higher recovery and grades were achieved from selective flocculation using sodium silicate and sodium oleate than was achieved from the combination of sodium silicate and starch.

2.3. Use of the separation efficiency (SE) and the selectivity index to evaluate separation

It has been shown that grade and recovery values can also be combined to generate other useful and alpha-insensitive indices to evaluate separation processes; these indices include separation efficiency (SE) and the selectivity index (SI). The SE, also called the Schulz's index, has been defined by (Irannajad et al. 2018) as the difference between the recovery of valuable mineral to the concentrate and the recovery of the gangue mineral to the concentrate.

$$SE = (R_{v.C} - R_{g.C}) \cdot 100$$
 (1)

It is apparent that by increasing $R_{\nu,C}$ and decreasing $R_{g,C}$, the SE will be increased. The values of SE are between 0 and 100. This index has been frequently used to technically evaluate separation processes.

It is interesting to note that the separation factors for two components in one product (Equation 1) and for one component in two products can be equivalent. For instance, the Hancock formula shown in Equation (2) is equivalent to Schulz's index shown in Equation (1) (Drzymala 2007).

$$SE = 10000 \left(\frac{(X_{v,F} - X_{v,T})(X_{v,C} - X_{v,F})}{X_{v,F}(X_{v,C} - X_{v,T})(100 - X_{v,F})} \right)$$
(2)

 $\$ $X_{v,F}, X_{v,T}$ and X_{vC} — are the value component contents in feed, tails and concentrate.

Gaudin proposed the selectivity index (SI) as the convenient measure of two-way separation (Gaudin 1939). The selectivity index is a geometrical mean of the relative rejections and relative recoveries of two components and it can be used for the better presentation of selectivity in separation and to evaluate the quality and quantity of separation between valuable minerals and gangue in concentration processes (Irannajad et al. 2018; Salmani Nuri et al. 2016). The selectivity index is defined by Equation 3.

$$SI = \sqrt{\frac{R_{v,C} \cdot R_{g,T}}{(1 - R_{v,C}) \cdot (1 - R_{g,T})}}$$
 (3)

Table 4 shows the calculated values for SI and SE for selective flocculation using the preferred sodium oleate and sodium silicate combination.

Irannajad et al. (Irannajad et al. 2018) and Salmani Nuri et al. (Salmani Nuri et al. 2016) indicate that the higher the value of the selectivity index (SI) and the separation efficiency

Table 4. Calculated values for SI and SE for selective flocculation using the preferred sodium oleate and sodium silicate combination Tabela 4. Obliczone wartości SI i SE dla selektywnej flokulacji przy użyciu preferowanego sodu

Sodium Silicate & Sodium Oleate	Cr ₂ O ₃ in conc, %	Cr ₂ O ₃ rec in conc, %	Conc yield,	Gangue in tails, %	Tails yield,	Gangue rec in tails, %	Gangue rec in conc, %	IS	SE
NaSiO ₃ 44g/ton _{slurry} :Flocnt 18g/ton _{slurry}	41.22	85.20	47.37	93.55	52.63	63.87	36.13	3.19	49.07
NaSiO ₃ 88g/ton _{slurry} :Flocnt 18g/ton _{slurry}	41.65	84.30	46.39	93.29	53.61	64.88	35.12	3.15	49.18
NaSiO ₃ 106g/ton _{slurry} :Flocnt 18g/ton _{slurry}	40.98	86.50	48.38	94.01	51.62	62.96	37.04	3.30	49.46
NaSiO ₃ 133g/ton _{slurry} :Flocnt 18g/ton _{slurry}	40.61	87.20	49.22	94.22	50.78	62.08	37.92	3.34	49.28
NaSiO ₃ 44g/ton _{slurry} :Flocnt 44g/ton _{slurry}	39.06	89.80	52.69	95.06	47.31	58.34	41.66	3.51	48.14
NaSiO ₃ 88g/ton _{slurry} :Flocnt 44g/ton _{slurry}	42.55	81.71	44.01	92.51	55.99	67.20	32.80	3.03	48.91
NaSiO ₃ 106g/ton _{slurry} :Flocnt 44g/ton _{slurry}	41.27	85.40	47.43	93.63	52.57	63.86	36.14	3.22	49.26
NaSiO ₃ 133g/ton _{slurry} :Flocnt 44g/ton _{slurry}	40.61	87.60	49.44	94.38	50.56	61.91	38.09	3.39	49.51
NaSiO ₃ 44g/ton _{slurry} :Flocnt 62g/ton _{slurry}	40.37	84.60	48.03	93.21	51.97	62.84	37.16	3.05	47.44
NaSiO ₃ 88g/ton _{slurry} :Flocnt 62g/ton _{slurry}	42.10	84.80	46.17	93.53	53.83	65.32	34.68	3.24	50.12
NaSiO ₃ 106g/ton _{slurry} :Flocnt 62g/ton _{slurry}	39.29	87.73	51.18	94.24	48.82	59.69	40.31	3.25	47.42
NaSiO ₃ 133g/ton _{slurry} :Flocnt 62g/ton _{slurry}	40.12	84.10	48.05	92.99	51.95	62.68	37.32	2.98	46.78
Cr ₂ O ₃ in feed, %	22.92								
Gangue components in Feed, %	77.08								

(SE) the higher the selectivity of these particular conditions in the upgrading of the value component in the concentrate. In the tests conducted using the flocculent (sodium oleate) and sodium silicate as dispersant. In the tests conducted at the flocculent (sodium oleate) dosage of 18 g/ton_{slurry}, the dispersant dosage of 106 g/ton_{slurry} gives the highest SI and SE. In the tests conducted at the flocculent (sodium oleate) dosage of 44 g/ton_{slurry}, the dispersant dosage of 133 g/ton_{slurry} gives the highest SI & SE. In the tests conducted at the flocculent (sodium oleate) dosage of 62 g/ton_{slurry}, the dispersant dosage of 88 g/ton_{slurry} gives the highest SI & SE. Considering all test-work conditions, the condition that gives the highest SI & SE is sodium oleate: 44 g/ton_{slurry} and sodium silicate: 133 g/ton_{slurry} suggesting that this condition is the most selective in upgrading the value component. The condition that gives the lowest SI & SE is sodium oleate 62 g/ton_{slurry} and sodium silicate 133 g/ton_{slurry} suggesting that this condition is the least selective in upgrading the value component. This analysis is in agreement with the results in Figure 9.

2.4. The effect of washing/decantation stages on flocculated mass grade

The flocculated mass was washed in a series washing and decantation stages in order to evaluate the effect that washing will have on grade. A series of settling and decantation tests were conducted at a flocculent (sodium oleate) dosage of 44 g/ton_{slurry} and a dispersant (sodium silicate) dosage of 88 g/ton_{slurry}, the reagent dosages that produced a flocculated mass of highest grade. In the experiment, after settling, the supernatant was decanted from

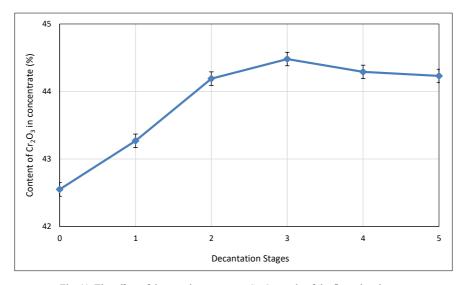


Fig. 11. The effect of decantation stages on Cr₂O₃ grade of the flocculated mass

Rys. 11. Wpływ etapów dekantacji na stopień Cr₂O₃ flokulowanej masy

the measuring cylinder and replaced by an equal volume of fresh solution with 88 g/ton_{slurry} dispersant. The measuring cylinder was then gently inverted three times to mix the settled solids with the fresh solution before the suspension was allowed to settle again. After each experiment, the flocculated mass was dried, sampled and chemically analyzed. The results of the grade of the settled solids as a function of decantation stages is shown in Figure 11.

As the number of decantation stages increase from one to three, there is a steady increase in the $\rm Cr_2O_3$ grade of the flocculated mass from the 42.55% to about 44.48%. This indicates that the washing is releasing the gangue trapped in the flocculated mass causing the $\rm Cr_2O_3$ content of the concentrate to increase. The increase in decantation stages from Stage 3 onwards does not improve the grade. A small decrease in the $\rm Cr_2O_3$ grade is observed suggesting that further washing does not result in any grade improvement but has a slight opposite effect. The reason could be that the flocs begin to be weaker and start to disintegrate after three stages causing previously aggregated mineral particles to be re-dispersed.

On an industrial scale, selective flocculation and the decantation washing process can be developed using a series of thickeners like the arrangement in counter-current decantation. A number of washing stages can be determined to give the target or desired quality of chrome concentrate at a reasonably high throughput typical of thickener throughputs.

Conclusions

Selective flocculation of chromite slimes from a chrome processing plant in the North-West province of South Africa was studied. Corn starch and sodium oleate were used as the flocculants and sodium silicate was used as a dispersant. In selective flocculation using sodium oleate, the results show that a maximum Cr_2O_3 content of the flocculated mass of 42.55% was obtained at a sodium silicate dosage of 88 g/ton slurry and a sodium oleate dosage of 44 g/ton_{slurry}. Flocculation using starch showed that the Cr_2O_3 content of the settled fraction was 35.92% min and 39.61% max. The Cr_2O_3 content of the flocculated mass was highest at a sodium silicate dosage of 106 g/ton_{slurry}. The best grade was recorded at the highest sodium silicate and starch dosage of 106 and 62 g/ton_{slurry}, respectively. The results showed that sodium oleate performed better than starch in achieving superior grades and recoveries of chrome in the flocculated mass.

Grade and recovery values in themselves do not directly correlate to the effectiveness of separation. They can, however, be combined to generate other useful and alpha-insensitive indices that better evaluate separation processes. In this work, the separation efficiency (SE) and the selectivity index (SI) were used to determine the conditions that offer the best upgrading conditions. The higher the value of the SI and SE the higher the selectivity of those particular conditions in the upgrading of the value component in the concentrate. Considering all test-work conditions, the condition that gave the highest SI & SE is sodium oleate: 44 g/ton_{slurry} and sodium silicate: 133 g/ton_{slurry} suggesting that this condition is the most selective in upgrading the value components. The condition that gives the lowest

SI & SE is sodium oleate: $62 \text{ g/ton}_{slurry}$ and sodium silicate: $133 \text{ g/ton}_{slurry}$ suggesting that this condition is the least selective in upgrading the value components.

Decantation washing tests showed that the chrome grade of the concentrate can increase to > 44%. These results are very encouraging and indicate that the selective flocculation can be used to recover chrome from the chrome slimes using relatively inexpensive reagents at low dosages.

There has been limited work done on chrome fines flocculation, particularly the flocculation of non-synthetic chrome slimes and the consideration of washing and decantation to enhance the flocculation process represents a significant incremental understanding of how this process can potentially be applied in industry.

The authors would like to acknowledge the chrome processing plant in the North-West province of South Africa for providing the chrome ore slimes for this investigation. The authors would also like to acknowledge the School of Chemical and Metallurgical Engineering at the University of Witwatersrand, South Africa for the provision of the reagents, laboratory equipment and the funding for the investigation.

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SELECTIVE FLOCCULATION AND RECOVERY OF CHROME FROM PLANT SLIMES USING STARCH AND SODIUM OLEATE AS FLOCCULANTS

Keywords

selective flocculation, chrome slimes, flocculent, dispersant, recovery, grade

Abstract

A steady global decline in the grade of chromite ores is causing an increase in the mining of low grade and complex ores. The processing of such low grade and finely disseminated ores results in the increased production of primary and secondary slimes. Slimes have very poor recovery performance in most conventional technology and are usually disposed of into tailings storage facilities (TSF). The historic slimes in the TSFs and those arising from most chrome production processes constitute potential recoverable chrome resources. In this study, the selective flocculation of slimes from a chrome processing plant in the north west province of South Africa was conducted using raw corn starch and sodium oleate as flocculants and sodium silicate a dispersant was applied on. Limited work has been reported on the flocculation of non-synthetic chrome slimes. The results showed that a slime sample with a chrome (Cr₂O₃) head grade of 22.92% was upgraded to a maximum concentrate grade of 42.55% at a sodium oleate dosage of 88 g/ton_{slurry}, a sodium silicate dosage of 44 g/ton_{slurry}, 39.61% at a starch dosage of 106 g/ton_{slurry} and sodium silicate dosage of 62 g/ton_{slurry}. The corresponding recoveries using sodium oleate as a flocculent were between 80-89% and 73-79% for starch. Sodium oleate showed a better performance than starch in terms of both grade and recovery. Decantation washing tests showed that the chrome (Cr₂O₃) grade of the concentrate can be further increased to above 44%. These results are very encouraging as they indicate that selective flocculation can achieve satisfactory upgrade ratios and recovery when processing chrome ultrafine or slime material.

SELEKTYWNA FLOKULACJA I ODZYSKIWANIE CHROMU ZE SZLAMÓW ZAKŁADÓW PRZEMYSŁOWYCH PRZY UŻYCIU SKROBI I OLEINIANU SODU JAKO FLOKULANTÓW

Słowa kluczowe

flokulacja selektywna, szlam chromowy, flokulant, dyspergator, odzysk, gatunek

Streszczenie

Stały spadek jakości rud chromitowych na całym świecie powoduje wzrost wydobycia rud niskogatunkowych i wielosurowcowych. Przeróbka tak niskogatunkowych i drobnouziarnionych rud powoduje wzrost ilości szlamów pierwotnych i wtórnych. Szlam ma bardzo słabą wydajność odzysku w większości konwencjonalnych technologii i jest zwykle umieszczany w osadnikach odpadów przeróbczych (TSF – Tailings Storage Facilities). Historyczne szlamy w TSF i te powstające w większości procesów produkcji chromu stanowia potencjalne zasoby chromu do odzyskania. W pracy przeprowadzono selektywną flokulację szlamów z zakładu przetwórstwa chromu w północno-zachodniej prowincji RPA, stosując surową skrobię kukurydzianą i oleinian sodu jako flokulanty oraz krzemian sodu jako dyspergator. Odnotowano ograniczoną liczbę prac nad flokulacją niesyntetycznych szlamów chromowych. Wyniki wykazały, że próbka szlamu o zawartości chromu (Cr₂O₃) 22,92% została ulepszona do maksymalnego poziomu koncentratu 42,55% przy dawce oleinianu sodu 88 g/tonę szlamów i krzemianu sodu 44 g/tone szlamów i 39,61% przy dawce skrobi 106 g/tone szlamów i krzemianu sodu 62 g/tonę szlamów. Odpowiednie odzyski przy użyciu oleinianu sodu jako flokulanta wynosiły od 80-89% do 73-79% dla skrobi. Oleinian sodu wykazał lepsze wyniki niż skrobia zarówno pod względem jakości, jak i odzysku. Testy płukania dekantacyjnego wykazały, że odzysk chromu koncentratu (Cr₂O₃) można dodatkowo zwiększyć do ponad 44%. Wyniki te są bardzo zachęcające, ponieważ wskazują, że selektywna flokulacja może osiągnąć zadowalające wskaźniki poprawy i odzysku podczas przetwarzania ultradrobnego lub szlamowego materiału chromowego.