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Dry magnetic separation of olivine sand

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Abstract. This paper investigates the potential for using dry magnetic separation to reduce the chromium content of a dried high quality olivine sand product in order to meet with anticipated future quality demands. The original feed contained 0.28-0.29% Cr_2O_3 of which approximately one third occurred as chromite and two thirds as chlorite. Two stage Permroll separation (at 0.50 T (max) and 0.92 T (max)) produced a concentrated product containing 0.13% Cr_2O_3 at a product recovery of 85.28%, thus reducing the chromium content by 55%. Some 80% of this reduction was achieved as a result of the first separation stage where chromite reported to the magnetic tailings at a recovery close to 100%. The chromium remaining in the concentrated product must be attributed to chlorite. Leachates obtained from leaching tests performed on the feed and the products were characterised by very low chromium concentrations, and the results suggest that chromium is more easily released from chlorite than chromite. This study shows that dry magnetic separation could be considered when a reduction of the chromium content of dried high quality olivine sand products is required.

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keywords: magnetic separation, Permroll, olivine, chromium, chromite, chlorite

1. Introduction

Due to its many favourable properties, olivine ($(Mg,Fe)_2SiO_4$) is a versatile industrial mineral which has found a number of uses. However, when excluding the domestic Japanese use of olivine for civil engineering purposes, the majority of the world's olivine production is consumed as slag conditioner by the metallurgical industry where the mineral is exploited for its high magnesium content (Skillen, 1995; Harben, 1999; Rudi, 2001, Roberts, 2008). Slag conditioner is a low-cost bulk commodity subject to relatively tolerant product specifications, and volume rather than grade has been seen as the key to success. Hence, the production lines comprise comminution and sizing, but little or no beneficiation. However, increasing competition, relatively low olivine prices and strong dependence on the fortunes of a single market have been an incentive for producers to diversify their product range. Entering into novel markets, producers are now facing a new set of specifications reflecting stricter demands on quality. As a consequence, mineral separation could to a greater extent become part of the production process.

Commercially, the term olivine could represent a range of different rock types including dunites, peridotites, serpentinites and sometimes even calcined products. Applying a mineralogical definition, olivine usually designates members of the continuous magnesium-iron solid solution series bound by the end-members *forsterite* (Mg_2SiO_4) and *fayalite* (Fe_2SiO_4) (Bowen and Schairer, 1935). The composition of olivines is frequently expressed in terms of the relative molar content (%) of forsterite (Fo_x) or fayalite (Fa_{100-x}). Forsterite (i.e. Fo_{90} to Fo_{100}) accounts for approximately 85% of commercial olivine (Harben, 1995; Roberts, 2008) and is predominantly produced from dunite, a rock defined as containing more than 90% olivine. In addition, dunites usually contain a range of accessory minerals such as enstatite, augite, anthophyllite, clinoamphiboles, talc, serpentine, phlogophite, chlorite and chromite. As a result, the overall chemical composition of the material could comprise heavy metals and other trace elements not found in the olivine lattice itself. This is the case for chromium, which is commonly present as chromite ($(Mg,Fe)Cr_2O_4$), in chlorite ($(Mg,Al,Fe,Cr)_{12}[(Si,Al)_8O_{20}](OH)_{16}$) or in even smaller amounts as a substitution element in the structures of amphiboles or phlogophites.

As explained in the first paragraph, olivine ores are subject to little or no beneficiation. However, some attempts have been made to reduce the Loss On Ignition (LOI) value of the product to improve the thermal stability of olivine sand used for foundry purposed. The LOI value (i.e. the relative weight loss when the sample is kept at 900°C for 30 min) can be attributed to the presence of minor amounts of chlorite and serpentine. Due to the flaky nature of the chlorite, dust removal by air classification (e.g. simple zig-zag sieves or classifiers) can produce a significant reduction of LOI value of sieved olivine sand products, typically from a value of 2% to 0.5% for a high quality olivine ore (Kleiv, 2001). At Åheim, the world's largest commercially exploited olivine deposit, some 5-10% of the feed to the sieving plant is removed as fines by air sweeping during sieving (Kleiv, 2001). Chmelar et al. (2003) used a SINTEF forced vortex Air Classifier to retrieve the olivine fraction from the fines, and demonstrated that the technology can be used to produce a fine sand product low in chlorite. The LOI value is closely correlated with content of aluminium, calcium and alkali oxides which are also unwanted in metallurgical applications. A successful alternative to air classification in order to lower the content of the latter constituents have been reported by Grishin et al. (2000) who used dry magnetic separation to produce a concentrated olivine middlings product. As for attempts to lower the chromium content of the olivine sands, little is reported in literature. As chromium frequently occur in olivine sands in both chromite and chlorite, air classification and magnetic separation could be considered.

During the last two decades, a number of new olivine applications have been developed based on the mineral's potential environmental benefits. This includes olivine for water treatment as an adsorbent for heavy metals (El Aamrani et al., 2002;

Kleiv and Sandvik 2002; Kleiv and Thornhill 2004, Bhakhar, 2006), dissolved natural organic matter (NOM) and microbial pathogens (McMeen and Benjamin, 1997), as well as olivine for the neutralisation of acid mine drainage (Morales and Herbert 2001; Kleiv and Thornhill, 2004, 2008) or waste acids (Schuiling, 1986; Herk et al., 1989; Jonckbloedt, 1998). Research is also being conducted on the use of olivine as a catalyst for the breakdown of tars in fluidised bed combustion reactors (Devi et al., 2005) and as an agent for carbon dioxide sequestration (Haug, 2010, and references within).

Some of these applications represent low cost bulk products, but others have the potential of becoming highly priced commodities that could easily defend the costs of additional beneficiation in order to meet with more stringent quality demands. This is particularly the case for the adsorbents and the catalysts, i.e. applications basing their value on the surface properties of the mineral rather than those of its bulk. Heavy metal adsorbents based on pellets, granulates or size fraction combining high reactivity with the necessary permeability could obtain prices up to several hundred USD per tonne. These environmental applications, including the somewhat lower priced olivine sand and olivine fines used for capping of polluted sediments as well as passive treatment of acid mine drainage and industrial seepage, represent a growing sector and are the focus point of this study.

Products used in water treatment or for environmental applications must in themselves be very low in heavy metals and other detrimental substances in order for their use to be approved by the relevant governmental regulatory bodies. Recently there has been growing concern with respect to the chromium content of olivine commodities and several new products are likely to face stricter compliance limits in the future. For both precautionary and practical reasons, regulatory limits are often based on the total contents of the substance in question and take little or no account of its state of occurrence or real potential for harm. Hence, even producers facing limitations on truly harmless products could, when possible, find it easier to perform the necessary separation rather than to fully verify their innocuous nature. As an example, the Norwegian Waste Directive (NME 2004) uses an elemental concentration limit (hereby referred to as the NWD-limit) of 0.1% for selected metals (corresponding to 0.146% Cr_2O_3) to determine whether a waste product should be classified as hazardous or not. Prior to depositing (or recycling) spent olivine based adsorbents and saturated filter media will probably have to comply with these limits as they no longer can be classified as production waste form mining, but will be subject to new classification and evaluation. Hence, in lack of concrete application specific limits for the new line of products, the NWD-limits could be used as a reference point and a preliminary target for the chromium concentration of olivine sand for environmental purposes.

To facilitate the strategy outlined in the previous paragraph, this paper investigates the potential for using dry magnetic separation to lower the chromium content in a high quality olivine sand product. The olivine sand in question is a dried and sieved standard product with a size distribution that is directly applicable for a several new high price applications. This would represent a typical situation for a number of producers working to expand their product portfolio. Consequently, a dry beneficiation method is preferred where the separation is performed on the material ‘as is’ without any preceding comminution.

Traditionally, the development of olivine applications has been spurred by the olivine producers (Kleiv, 2001), and it is here the results presented in this paper could be utilised. However, due to the interdisciplinary nature of the new environmental products and applications (spanning from mineralogy, surface science and geochemistry to toxicology and civil engineering), cooperation with research institutions, universities and consultancy firms will usually be required to achieve results. Such cooperation is also necessary to get access to the new markets as these can be very divers and governed by different mechanism than the traditional olivine markets. As an example, target customers for olivine based adsorbents would include both industry and public authorities with markets ranging from municipal water treatment plants, treatment of acid mine drainage problems from disused mines, run off from shooting ranges, metallurgical industry, sand blasting facilities, garages and tool shops, as well as remediation of polluted soil and sediments.

2. Materials and methods

2.1. Chemical and mineralogical analysis

The chemical composition of solid samples was determined by x-ray fluorescence (XRF) analysis using a Bruker AXS S8 Tiger wavelength dispersive spectrometer. Main element and trace element analysis were obtained using pressed powder disks and glass disks, respectively. All analyses were calibrated against dunite standards. Analytical detection (i.e. qualitative analysis) of specific mineralogical phases was obtained through X-ray powder diffraction analysis (XRD), using a Bruker D8 Advance diffractometer with a Krystalloflex K780 generator, scanning from 2° to 70° (2θ) with monochromatised CuK_α radiation. The pulverised material required for the XRF and XRD analysis was produced by 30 s milling in a Siebtechnik agate disk mill. Great care was taken to minimise the risk of cross-contamination between samples.

The chemical composition of filtrates from the leaching test were analysed by inductively coupled plasma mass spectrometry analysis (ICP-MS) using a PerkinElmer DRCII ICP-MS equipped with a dynamic reaction cell.

2.2. The original olivine sand sample

The olivine sand used in this study was kindly supplied by the Norwegian mining company *A/S Olivin* and originates from the production plant at Åheim in western Norway. The material is a standard foundry sand produced by crushing, drying and sieving the dunite ore. Prior to sieving, are removed by air sweeping, thus leaving a purified product containing almost 95% forsterite olivine. The particular foundry sand used in this study consists of well sized material ranging from $d_5 = 150$ µm to $d_{95} = 390$ µm. The original sample was delivered as a single 25 kg bag. All subsamples used for characterisation or separation experiments were carefully split out from this batch.

Table 1. Feed assay obtained from XRF analysis

Constituent	Assay, %
MgO	49.7
SiO_2	41.5
Fe_2O_3	7.23
Al_2O_3	0.72
NiO	0.33
Cr_2O_3	0.29
CaO	0.26
MnO	0.09
K_2O	0.03
Na_2O	0.01
LOI	0.29
Sum	100.45

The geology, mineralogy and mineral chemistry of the Almklovdalen ultramafic massif from which the olivine sand originates has been described in detail by Osland (1998). The 8 km^2 ring-shaped exposure of the massif displays a continuous layering of dunite, chlorite-bearing and chlorite dunite, blastogranular dunite and Fe-rich eclogites. Whereas the composition of the olivine exhibits a slight variation through the different layers with MgO contents ranging from 48% to 51% in the dunites, its average composition can be represented by $Mg_{1.86}Fe_{0.14}SiO_4$ (i.e. Fo_{93}). In addition to the olivine, the dunites also contain minor quantities of accessory minerals such as chlorite, enstatite, calcic amphiboles, serpentine, talc, and chromite. Table 1 shows the chemical composition of the original olivine sand sample as obtained from XRF analysis.

Based on these results, employing the mineralogical data and the principles and assumptions described in section 2.6, the respective content of chlorite and chromite in the original olivine sand sample was found to be approximately 5.3-5.6% and 0.1-0.2%. This suggests that approximately one third of the total chromium content can be attributed to chromite.

2.3. Frantz separation

To provide an initial assessment of the relative magnetic susceptibility distribution of the original olivine sand sample a standard Frantz LB-1 isodynamic laboratory magnetic separator was used to produce a total of nine successively less magnetic fractions from a feed sample of 988 g. Each successive magnetic fraction was obtained from a single pass. The nine fractions were all subjected to XRF analysis. The separator was operated with a side slope of 7° and a forward tilt of 10°.

2.4. Permroll separation

A 6555 g subsample of the original olivine sand sample was subjected to dry magnetic separation in two stages using two laboratory Permroll separators with different effective field strengths. The diameter and width of the rolls were 90 mm diameter and 130 mm, respectively. Based on the results from the Frantz separation (see section 3.1), the separation flowsheet (Fig. 1) was designed to produce a cutpoint at either end of the susceptibility range, thus producing a concentrated olivine product.

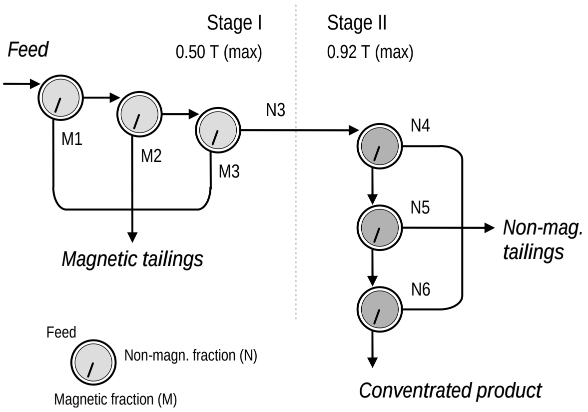

Fig. 1. Flowsheet for Permroll separation

The effective field strengths of the separators were estimated using a Hirst GM05 Gaussmeter equipped with a transverse P3110 Hall effect probe. The respective maximum flux densities of the stage I and stage II separators, as measured on the belt, were found to be approximately 0.50 T and 0.92 T.

The first separation stage, removing the magnetic tailings, consisted of three consecutive runs where the nonmagnetic fraction (i.e. as defined by the separation) from the first became the feed to the next. The mass of the magnetic fraction from each run (M1 to M3) was determined before the subsamples were split out for XRF-analysis. The remaining mass was mixed in the correct proportions to achieve a combined magnetic tailings product that could be submitted to the leaching test. The remaining nonmagnetic fraction (N3) reported to the second separation stage where the separation was conducted according to the same pattern, but with the removal of the consecutive nonmagnetic (N4 to N6) rather than magnetic fractions. As with the first separation stage, the mass of these outputs was determined and analytical samples were obtained before the material was recombined.

Prior to each of the two stages the position of the separating knife and the speed of the separator were adjusted until a clear cut was produced at the desired cut point. During the first stage the separator was operated at a speed of 120 rpm, whereas a speed of 190 rpm was used during the second stage. The feed rate was kept constant at 120 kg/h per metre roller width during both stages.

2.5. Leaching tests

In order to determine the effect of the magnetic separation on the leaching potential of the concentrated product as well as to assess the relative mobility of chromium in the different separation products, the original feed, the concentrated product and the two combined tailings materials were all subjected to a leaching test according to the procedure given in EN-12457-2 (CEN, 2002). This is a compliance test that was originally developed for the testing of waste materials. Due to its simplicity, variations of the test have later been used for range of purposes.

The leaching tests were performed using clean HDPE bottles as reactors by mixing 90 g of dry solid sample with 900 cm^3 of distilled water, thus establishing a liquid to solid ratio of 10:1. The resulting suspensions were agitated at room temperature for 24 hours using an end-over-end sample agitator. On completion of the agitation period, the pH of the suspensions was determined using a Metrohm 713 pH Meter equipped with an Aquatrode Plus combined glass electrode (spherical bulb). A 10 cm^3 sample of each suspension was then retrieved by syringe and filtered using serially connected disposable 0.45 μm and 0.20 μm syringe filters. The filtrates were collected in glass vials and acidified by adding 20 μl of 65% suprapure nitric acid. Finally, the filtrates were analysed using the ICP-MS technique as described in section 2.1. Great care was taken to minimise the risk of contamination throughout the test and during the subsequent handling of the filtrates.

2.6. Estimating mineralogical composition

To aid in the interpretation of the separation results, the content of chlorite and chromite in each sample was estimated based on its chemical assay and the average chemical composition of each mineral. These calculations were based on the simplifying assumption that chlorite and chromite were the only minerals present that contribute significantly to the total amount of aluminium and chromium that can be found in a sample. As shown by Osland (1998), this is truly the case for chromium, whereas aluminium could also occur in minor amounts in calcic amphiboles or in phlogophite. The contribution from the latter could be ignored as significant amounts of this mineral would produce elevated potassium assays, a feature not encountered in any of the samples. A small amount of calcic amphibole was probably present as indicated by the 0.26% CaO found in the feed. However, as the amphibole most likely would report to the non-magnetic tailings due to its low iron content (approximately

2% FeO_{tot}), the simplifying assumption was expected to be reasonable when applied to the feed or to fractions where chromite is present.

Based on microprobe analysis, Osland (1998) found that the Cr_2O_3 content in the chromite varied from 51% to 62% with 58% as an estimate of the average. The analysis also showed 26-31% FeO_{tot} and 6-9% MgO, whereas the average chromite contained approximately 3.7% Al_2O_3 (varying from 2.4% to 4.2%). The chlorite contained on average 3.6% Cr_2O_3, with values ranging from 3.1% to 4.3%, whereas the estimated average Al_2O_3 content was found to be 13.6% (varying from 12% to 15%). The chlorite also contained some 2-3% FeO_{tot} and 33-34% MgO.

The relative error between the true assay a_i of a sample (i.e. the assay value for oxide i obtained from XRF analysis) and the assay value that can be calculated by assigning values to the samples content of chlorite and chlorite can be defined as:

$$\varepsilon_i = \frac{a_i - \sum_j g_{ij} x_j}{a_i} \quad , \tag{1}$$

where x_j is the relative amount of mineral j in the sample and g_{ij} is the assumed average concentration of oxide i in mineral j. The best estimates for $x_{chlorite}$ and $x_{chromite}$ where found by minimising the sum of $(\varepsilon_i)^2$ for the two oxides Al_2O_3 and Cr_2O_3. Note that estimates are given to two decimal places simply in order to facilitate internal comparison, and that his does not in any way reflect their level of accuracy. The reported values must only be seen as semi-quantitative estimates.

3. Results and discussion

3.1. The magnetic properties of the feed

Table 2 presents the complete data from the Frantz separation, including the current applied during separation, the assays of each successive fraction and the estimated mineralogy derived from the latter. Note that the estimates for the contents of chlorite and chromite are calculated directly from the assays of each respective fraction, and that no attempt has been made to achieve a normalised mineralogical mass balance. From the data displayed in Table 2 it is clear that chromium is enriched in the fractions at either end of the magnetic susceptibility range, with some 30% of the total content found in the most magnetic fraction representing only 5% of the total mass. This feature is illustrated in Fig. 2 where the cumulative chromium distribution is shown. Note the logarithmic scale of the ordinate axis.

The estimated mineralogy suggests that chromium reports to the most magnetic fractions and that the least magnetic third of the material is virtually chromite free. Chlorite shows the opposite trend, although some chlorite appears to occur in every fraction. The relative estimation error ε_i is very low for the six first fractions, i.e. as long as chromite is present. Beyond this point, the estimated mineralogy will underestimate the aluminium content of the material. Here, as expected, the assumption that chlorite represents the only significant aluminium-bearing mineral is no longer valid.

A simple qualitative XRD analysis was performed on the original olivine sand sample (i.e. the feed) and the F1, F5 and F9 fractions. The results supported the picture displayed by the estimated mineralogy as it was impossible to detect chromite in the F9 fraction, whereas chlorite could be detected in all the analysed samples. Chromite was clearly enriched in the F1 fraction and marginally present in F5 and the feed. The many overlapping diffraction peaks of forsterite and the fact that both chlorite and chromite only occur as trace minerals made it impossible to use XRD as a tool to quantify mineralogy. Hence, in spite of its obvious flaws, the model described in section 2.6 provides a better initial estimate.

Table 2. Results from Frantz separation. The chemical composition is obtained from XRF analysis

Fraction	Current[a]	Mass distr.	Cr distr.	Chemical composition		Estimated mineralogy		Relative error ε_i [%]		% Cr as
	[A]	[Cum.%]	[Cum.%]	[%Al_2O_3]	[%Cr_2O_3]	[%chlorite]	[%chromite]	in Al_2O_3	in Cr_2O_3	chromite
F1	0.230	0.50	12.3	2.03	7.39	11.40	12.96	0.0	0.0	94.8
F2	0.293	4.35	28.9	0.39	1.30	2.30	2.10	0.1	0.1	93.6
F3	0.311	10.38	37.4	0.33	0.42	2.27	0.58	0.1	-0.4	80.5
F4	0.318	23.79	46.8	0.54	0.21	3.93	0.12	-0.2	0.5	33.0
F5	0.339	47.33	63.4	0.51	0.21	3.72	0.13	0.1	-0.3	36.0
F6	0.358	71.95	80.1	0.74	0.20	5.42	0.01	-0.3	0.5	2.9
F7	0.381	93.64	94.9	0.98	0.20	6.17	0	-14.4	11.1	0
F8	0.400	96.50	97.0	1.34	0.23	7.41	0	-24.8	16.0	0
F9	0.410	100	100	1.89	0.26	8.64	0	-37.8	19.6	0

[a] Applied current during separation

The bipolar chromium distribution must be attributed to the differences in specific magnetic susceptibility between the two chromium-bearing minerals and the olivine itself. The mass magnetic susceptibility of olivine is known to be a function of the mineral's iron content, with the fayalite (Fe_2SiO_4) end-member being the most magnetic. Hopstock (1985) gives a range of $0.11–1.26 \cdot 10^{-6}$ m^3/kg, whereas Grishin et al. (2000) reports a value of $0.226 \cdot 10^{-6}$ m^3/kg for Fo_{92}. In a more recent study, Belley et al. (2009) found that the pure forsterite (Mg_2SiO_4) end-member is diamagnetic and suggests a range from $–6.8 \cdot 10^{-10}$ m^3/kg to $1.10 \cdot 10^{-6}$ m^3/kg. However, as shown by Belley et al. (2009), the susceptibility does not vary linearly with iron content and the interpolated approximate value of $0.15 \cdot 10^{-6}$ m^3/kg for Fo_{93} is in agreement with the data presented by Hopstock (1985) and Grishin et al. (2000). Turning to chromite, the reported values for mass magnetic susceptibility shows a much wider range, clearly reflecting the compositional variation that can be found within the spinel structure. As pointed out by Svoboda (1987), the existence of contradictory reports prevents a simple correlation with the mineral's magnetite content (i.e. the content of ferric iron). Whereas Hopstock (1985) reports a very narrow range of $0.32\text{-}0.38\cdot10^{-6}$ m^3/kg, Svoboda (1987) presents a range of values starting at $0.5\cdot10^{-6}$ m^3/kg spanning four orders of magnitude. Mass magnetic susceptibility values for chlorite proved difficult to obtain. Grishin et al. (2000) does not give direct information, but provides values for phlogophite and muscovite (i.e. other sheet silicates) that are 55-85% lower than that of Fo_{92}. In their study on magnetic separation of olivines form the Kola peninsula, Grishin et al. (2000) found that all the accessory minerals apart from magnetite where less magnetic than the forsterite olivine.

Based on the results from the Frantz separation, the separation results reported by Grishin et al. (2000) as well as the susceptibility data reported in literature, it was reasonable to assume that magnetic separation could be employed to produce a concentrated Fo_{92} olivine middlings product with chromite reporting to the magnetic tailings. The results of Table 2 suggest a considerable overlap in magnetic susceptibility between the olivine and the chromium-bearing minerals, particularly in the case of chlorite, but it must be kept in mind that the successive fractions are obtained from a single pass at each step in the current applied to the separator. An even more polarised distribution was expected from the Permroll separation where three successive runs would be conducted at each cut point.

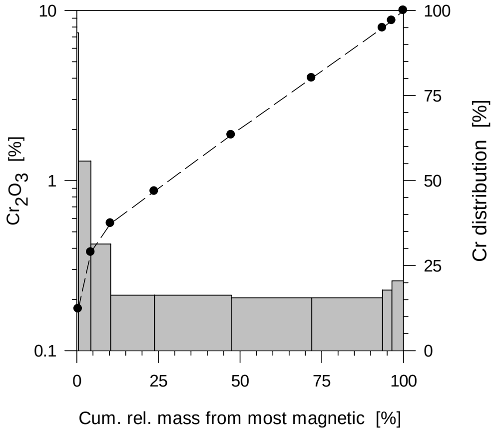

Fig. 2. Chromium distribution obtained from Frantz separation

3.2. The effect of Permroll separation

The results from the Permroll separation are shown in Table 3. Here, the chemical composition of the feed and the two (combined) tailings products is calculated based on the analysis of the recovered product and the yields and assays of the respective fractions from each individual run (i.e. M1 to M3 and N4 to N6). As shown in Table 3, the data set displays a fair agreement between the calculated and analysed feed composition. The total loss of material during separation was found to be 0.23%. As with the results from the Frantz separation, no attempt has been made to achieved a normalised mineralogical mass balance.

Table 3. Results from Permroll separation. The chemical composition is obtained from XRF analysis unless otherwise indicated.

Process stream	Mass distr.[a]	Cr distr.[a]	Chemical composition		Estimated mineralogy		Relative error ε_i [%]		% Cr as
	[%]	[%]	[% Al_2O_3]	[% Cr_2O_3]	[% chlorite]	[% chromite]	in Al_2O_3	in Cr_2O_3	chromite
Feed (analysed)	-	-	0.72	0.29	5.27	0.17	0.4	-0.6	34.2
M1	3.29	41.0	0.83	3.43	4.57	5.63	0.0	0.0	95.2
M2	1.13	3.9	0.42	0.96	2.68	1.49	-0.1	0.1	90.0
M3	0.43	0.6	0.26	0.38	1.76	0.55	-0.1	0.6	83.4
N3 (stage II feed)	(95.14)	(54.5)	0.75	0.17	5.06	0	-8.2	7.2	0
N4	3.27	4.9	2.32	0.41	13.14	0	-23.0	15.4	0
N5	3.33	5.1	2.19	0.42	13.19	0	-18.1	13.1	0
N6	3.25	4.3	1.96	0.37	11.67	0	-19.0	13.5	0
Feed (calculated)	100	100	0.77[b]	0.28[b]	5.59	0.13	-0.1	0.2	27.3
Magnetic tailings	4.86	45.5	0.68[b]	2.58[b]	3.85	4.21	-0.1	0.0	94.6
Nonmag. tailings	9.86	14.3	2.16[b]	0.40[b]	12.68	0	-20.2	14.1	0
Conc. product	85.28	40.2	0.61	0.13	3.95	0	-11.9	9.4	0

[a] Based on recovered mass, ignoring loss

[b] Calculated from mass balance

The concentrated olivine product from the Permroll separation contained 0.13% Cr_2O_3 at a recovery of 85.28%, which corresponds to a 54-55% reduction in the chromium content depending on the chosen value for the feed composition (i.e. the analysed value of 0.29% Cr_2O_3 or the 0.276% Cr_2O_3 derived from the calculated mass balance for chromium). This brings the concentrated product in compliance with the NWD-limit for classification as non-hazardous waste (i.e. less than 0.146% Cr_2O_3).When analysing the data given in Table 3, it is clear that some 80% of this reduction can be attributed to the first separation stage. Fig. 3 shows the relationship between the cumulative product recovery and the resulting product quality for the successive removal of the individual fractions M1 to M3 and N4 to N6.

The tailings from the Permroll separation consists mainly of olivine and their comparatively small volumes could therefore easily be mixed with the much larger volumes of slag conditioner and sold as such. At A/S Olivin’s deposit at Åheim, approximately 85% of the roughly 2 million tonnes of broken olivine ore is sold as slag conditioner. Slag conditioner is a low cost product that allows little beneficiation, but the product's tolerant specifications and large production volumes offer olivine producers a very favourable opportunity to turn the much smaller volumes of off-spec olivine, fines and alternative process tailings in to sellable products (Kleiv, 2001). Hence, as long as the concentrated olivine product from the Permroll separation can justify the separation costs, the corresponding tailings will only add positively to the economic balance.

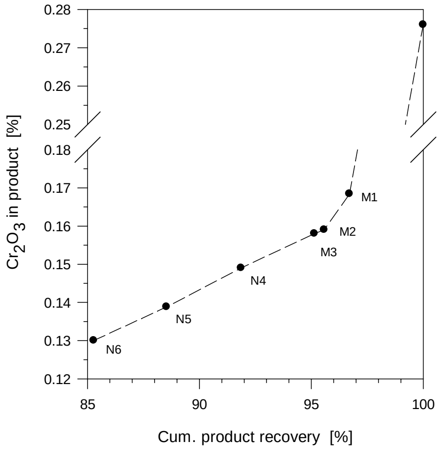

Fig. 3. Product quality as a function of cumulative recovery

As suggested by the estimated mineralogy as well as the rapid decrease in both the yield and chromium assays of the successive magnetic fractions from the first separation stage, the chromite is easily removed, thus leaving a virtually chromite free product. This conclusion is supported by the fact that the simple qualitative XRD analysis was unable to detect chromite in the concentrated product. As expected, the three successive runs performed during the first separation stage resulted in a much better concentration of chromium than was achieved during the Frantz separation. If only a single run had been conducted, an additional 4.5% of the total chromium present in the feed would have ended in the concentrated product.

Less efficient separation was achieved with respect to chlorite, as evident from the near constant yields and assays of the N4, N5 and N6 fractions. In spite of a significant enrichment in the non-magnetic tailings, chlorite appears to occur in all fractions. The possible compositional variations aside, chlorite is inherently a more problematic mineral to reject due to its flaky particle shape. This feature promotes pinning to the separator belt due to adhesive forces, as well as entrapment caused by more magnetic particles. Hence, a further reduction in the chromium content of the concentrated product would probably result in a significantly reduced recovery. The recovery of chlorite in the non-magnetic tailings was probably between 20% and 30%.

The total dissolved chromium concentrations in the filtered leachates from the leaching test are presented in Table 4. The values are very low and in the concentration range usually regarded as the geochemical background of natural waters. In comparison, the current US-EPA maximum contaminant level goal (MCLG) for chromium in drinking water is 0.1 mg/L. Being almost three orders of magnitude lower than the theoretical solubility of chromium hydroxide (Stumm and Morgan, 1996) the concentrations are probably controlled by kinetic factors and the availability of easily leachable surface sites. At first sight the values appear to show little variation, and it is evident that the 34% reduction in the leachate concentration achieved by Permroll separation is smaller than the corresponding reduction in the solid assays. However, the results clearly indicate the difference in relative leachability of the chlorite and the chromite. The concentration obtained for the 'chromite concentrate' is not much higher than that of the non-magnetic tailings even though the former contains 6.45 times more chromium than the latter. The higher leachability of the chlorite is also evident from the results obtained for the feed to the second separating stage (i.e. the N3 fraction). After the first separation stage has lowered the chromium concentration by more than 40%, the material still produces a leachate concentration only 17% lower than that obtained for the feed.

Table 4. Chromium concentration (C_{cr}) and pH in the leachates

Process stream	Assay [%Cr_2O_3]	pH	C_{Cr} [µg/L]
Feed	0.28[a]	9.23	0.86
N3 (stage II feed)	0.16[a]	9.42	0.71
Magnetic tailings	2.58[a]	9.05	1.14
Non-mag. tailings	0.40[a]	9.34	0.97
Concentrated product	0.13	9.49	0.57

[a] Calculated from mass balance

As shown by this study, a single separation stage, removing the chromite, goes a long way with respect to reducing the chromium content of the original olivine sand as it is responsible for some 80% of the total reduction achieved by the separation circuit. In applications were the foundry sand is used as an additive or a reactive agent in mixtures or composites and where its relative concentration in the receipt is limited by restrictions on the chromium content, the removal of chromite could allow the use of an additional 80-85% product mass. This could be of great practical importance for applications such as adsorbents and catalysts where the effect is strongly related to the concentration of the active phase or reagent. When facing restrictions with respect to the total chromium content even a small reduction could be of vital importance if it brings the product within the limits of tolerance. Hence, even the much less efficient second stage should be considered if the additional reduction is needed.

The second separation stage of the proposed flowsheet becomes more important if compliance with restrictions placed on aqueous concentrations is an issue, as approximately half the reduction in the leachate concentration can be attributed to the removal of chlorite. It is beyond the scope of this paper to assess the relative mobility of chromium as a function of its mineralogical occurrence or the pH and composition of the leachant to which the materials are exposed. However, as one would expect based on their different structures, the study indicates that the two chromium-bearing minerals could possess quite different leaching characteristics. Consequently, in spite of and as a contrast to the general and often indiscriminate nature of compliance limits, a more comprehensive approach is needed to optimise the beneficiation of the initial olivine sand products.

4. Conclusions

The following conclusions were reached based on the results from the Frantz and Permroll separation performed on the original olivine sand sample and the subsequent EN-12457-2 leaching test performed on the feed, product and tailings.

- The original olivine sand sample contained 0.28-0.29% Cr_2O_3 of which approximately one third occurred as chromite and two thirds as chlorite. These two minerals were enriched at either end of the sample's magnetic susceptibility range, thus enabling the production of concentrated olivine middlings.
- The two stage Permroll separation produced a concentrated product containing 0.13% Cr_2O_3 at a product recovery of 85.28%, thus reducing the chromium content by 55% and bringing the product in compliance with the NWD-limit for classification as non-hazardous waste (i.e. less than 0.146% Cr_2O_3). Some 80% of this reduction was achieved as a result of the first separation stage where chromite reported to the magnetic tailings at a recovery close to 100%. Hence, the chromium remaining in the concentrated product must be attributed to chlorite. The recovery of chlorite in the non-magnetic tailings was probably between 20% and 30%.
- The leachates were characterised by very low chromium concentrations. The concentrated product produced a value of 0.57 μg/L as opposed to the 0.86 μg/L produced by the feed. The results suggest that chromium is more easily released from chlorite than chromite. Hence, if a lower leachate concentration will be required, more chlorite will have to be removed from the concentrate. As the results indicate, this will be difficult to achieve with magnetic separation without sacrificing recovery.
- The study shows that dry magnetic separation should be considered when a reduction of the chromium content of dried high quality olivine sand products is required even though the potential enhancement is limited by the overlapping magnetic susceptibilities of olivine and chlorite.

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