FROM THE MINERAL TO THE COMMODITY: AN INNOVATIVE TECHNIQUE (DM + IFS) FOR THE PRODUCTION OF REFRACTORY CHROMITE

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INTRODUCTION

This work deals with disseminated chromite ore samples collected at Krasta Mine, located in the central-southern part of the Bulqiza Massif (Mirdita ophiolite, Albania). First of all the samples, having an average Cr_2O_3 content of 23.66 wt.%, were enriched using spirals and shaking tables at Krasta plant. The first chromite sand concentrate had 46.58 wt.% Cr_2O_3 and 10.35 wt.% SiO_2.

In order to meet the very demanding chemical parameter requirements for refractory market, chromite first concentrate sand was re-enriched using a combination of dry magnetic and gravity separation at the pilot plant of Omega Foundry Machinery LTD. in Peterborough (UK). After the first step carried out at Krasta plant, in the second step, carried out at Peterborough, the sand was enriched using a drum magnet (DM). New concentrate was then enriched in a third step by means of an Inclined Fluidised Separator (IFS) that works in dry conditions using an air cushion as fluidisation agent.

Preliminary results show that the pilot plant is able to strongly re-enrich the primary concentrate sand, producing a final concentrate sand with up to 60.01 wt.% Cr_2O_3 and as low as 2.43 wt.% SiO_2 with a tail that is still suitable for the steel market.

GEOLOGY OF THE MIRDITA OPHIOLITE

The Albanian ophiolites occur within the Dinaride–Hellenide segment of the Alpine orogenic system and represent the remnants of the MesozoicNeo-Tethyan ocean (*e.g.*, Shallo & Dilek, 2003; Dilek & Furnes, 2009).

The Mirdita ophiolite is located in the northern ophiolite belt of Albania (Fig. 1). Based on differences in the internal stratigraphy and chemical composition of the crustal unit, two types of ophiolites have been recognized in the Mirdita ophiolite, namely the Western Mirdita Ophiolite (WMO) and the Eastern Mirdita Ophiolite (EMO) (Beccaluva *et al.*, 1994; Bortolotti *et al.*, 1996; Dilek *et al.*, 2008; Shallo, 1990; Shallo *et al.*, 1987, 1990). Boninitic dikes and lavas crosscut and/or overlie earlier extrusive rocks in the EMO Beccaluva *et al.*, 1994; Dilek *et al.*, 2008; Shallo *et al.*, 1987).

The crustal section of the WMO has MORB affinities, whereas that of the EMO shows predominantly SSZ geochemical affinities. The extrusive sequence in the EMO consists of pillowed to massive flows ranging in composition from basalt and basaltic andesite in the lower section to andesite, dacite, and rhyodacite in the upper part (Bortolotti *et al.*, 1996; Dilek *et al.*, 2008). Large peridotite massifs are exposed at the western and eastern ends of the Mirdita ophiolite. Plagioclase-bearing peridotites are frequently observed in the WMO, whereas harzburgite is dominant in the EMO (Beccaluva *et al.*, 1994, 1998; Beqiraj *et al.*, 2000; Hoxha & Boullier, 1995).

BULQIZA MASSIF AND KRASTA CHROMITE DEPOSIT

Bulqiza Massif is located about 40 km North-East of Tirana (Fig. 1) and it is the most important ultrabasic complex hosting chromite ores of the EMO. It covers an area of 370 km^2 and the chromite reserves are currently estimated around 12 million tons.

Systematic lithological variations in the mantle section with proximity to the crustal section have previously been recognized (Beccaluva *et al.*, 1998; Beqiraj *et al.*, 2000; Hoxha & Boullier, 1995).
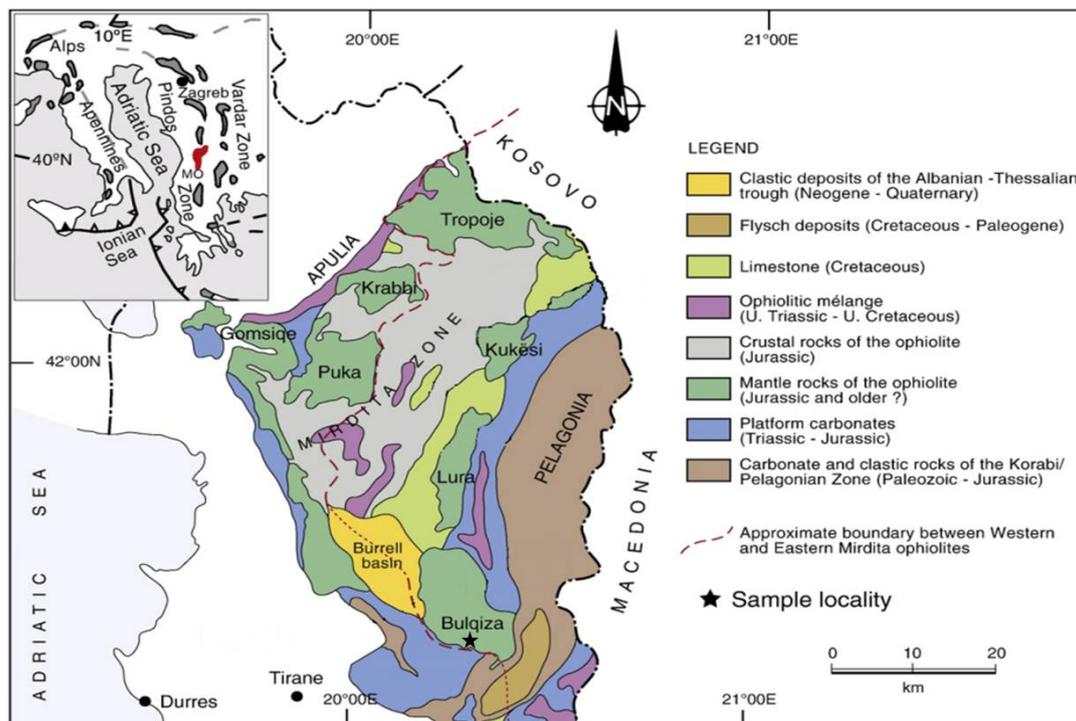
Fig. 1 - Simplified geological map of the Mirdita ophiolite in north-central Albania (modified from Dilek *et al.*, 2008) with position of sampling locality within Bulqiza massif. Inset map shows the distribution of a part of the Tethyan ophiolites in the Balkan Peninsula, with the Mirdita ophiolite in red.

We also confirmed systematic lithological variations in the mantle section: clinopyroxene porphyroclast-bearing harzburgites (Cpx-harzburgites hereafter, Fig. 2a) are sometimes observed in the eastern margin of massifs, *i.e.*, the basal part of the mantle section, whereas harzburgite and dunite are dominant in the upper parts of the mantle section (Beccaluva *et al.*, 1998; Beqiraj *et al.*, 2000; Dilek & Morishita, 2009; Hoxha & Boullier, 1995). Cpx-harzburgites have a porphyroclastic texture; clinopyroxene occurs as both porphyroclastic grains and their recrystallized fine grains. The lithological boundary between dunites and harzburgites is usually sharp and is sometimes nearly parallel to the foliation plane defined by mineral orientations. Dunite also frequently occurs as small bodies with complicated irregular boundaries with harzburgites (Fig. 2b). Harzburgite shows granular to porphyroclastic textures.

Orthopyroxenite dikes/layers (a few cm to 3 m wide) are frequently observed in the uppermost section of the mantle sequence (Beccaluva *et al.*, 1998; Dilek & Morishita, 2009; Fig. 2d). They rarely occur as layers nearly parallel to the foliation and lithological boundaries in the host peridotites, and more frequently occur as dike-like features cutting all lithological boundaries at high angles (Fig. 2b), indicating that they are related to late melt migration through the mantle section. Fewer deformation textures are observed in orthopyroxenites.

Orthopyroxenites mainly consist of coarse-grained orthopyroxene (up to 10 cm across) with small amounts of spinel and olivine. Olivines sometimes show resorbed textures in large orthopyroxene grains (Fig. 3b). Large orthopyroxenes have many clinopyroxene exsolution lamellae. Dark brown spinel is commonly included in large orthopyroxene grains. Orthopyroxenites locally contain amphibole and/or clinopyroxene. Clinopyroxene sometimes occurs as veins along orthopyroxenites. Amphibole occurs as an interstitial phase along the grain boundaries of orthopyroxene and also as poikilitic phases including orthopyroxene grains (Fig. 3c).
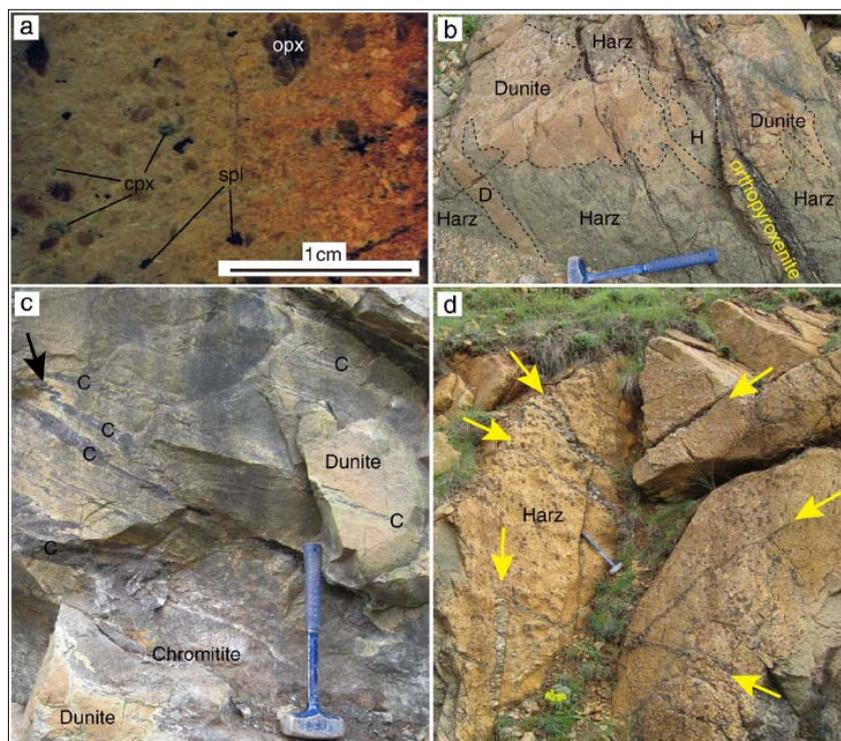
Fig. 2 - (a) Polished surface of a clinopyroxene porphyroclast-bearing harzburgite. (b) Field relationships between dunite, harzburgites and orthopyroxenite. (c) Occurrence of chromitite layers in dunite. Chromitite is sometimes tightly folded (arrow). (d) Orthopyroxenite network (yellow arrows) in harzburgites. C = chromitite, cpx = clinopyroxene, D = dunite, H or Harz =harzburgite.

Harzburgites and minor dunite layers and lenses, with different degree of serpentinization, host Krasta chromite ore that is located in the central southern part of the Bulqiza Massif (black star in Fig. 1). Outcropping chromitite layers a few centimeters thick are frequently observed in dunite and usually occur parallel to each other and to the lithological boundary between dunite and harzburgite (Fig. 2c). Chromitite layers are occasionally tightly folded in dunites (Fig. 2c). It is interesting to note that inclusions of silicate minerals, such as amphibole, orthopyroxene, clinopyroxene, and their secondary minerals (*e.g.*, chlorite and serpentine), are commonly found within chromian spinels in harzburgites near dunite (Fig. 3a).

Several chromite lumpies from Krasta mine stock were collected and XRF whole rock analysis reveals an average Cr_2O_3 content of 23.66 wt.%.

KRASTA ENRICHMENT PLANT

The Krasta mine has been exploited mainly in underground but also in open pit since 1971. Chromite sand (grain size = 1.5 mm) is produced at the Krasta enrichment plant, located in an optimum logistic position, being only a few meters from underground working adits.

Chromite sand enrichment is achieved by crushing and gravity separation. Crushing and grinding plant is composed of jaw and ball mills, with associated sieves and cylindrical rotating sieve, that reduce feed in the first step to -50 mm grain size and finally to -1.5 mm grain size.

Gravity separation plant is made up of spirals and shaking tables. Several pipes send feed to a series of spirals comprising 32 spirals. Each spiral produces three types of materials: concentrate, mix and waste. The mix material coming out from spirals is re-enriched by 8 shaking tables that produce concentrate and waste materials.

Concentrate sands obtained from spirals and shaking tables are blended in order to achieve the chromite final product that is stocked close to the plant while wastes from spirals and tables form tailings that are disposed in a dump.
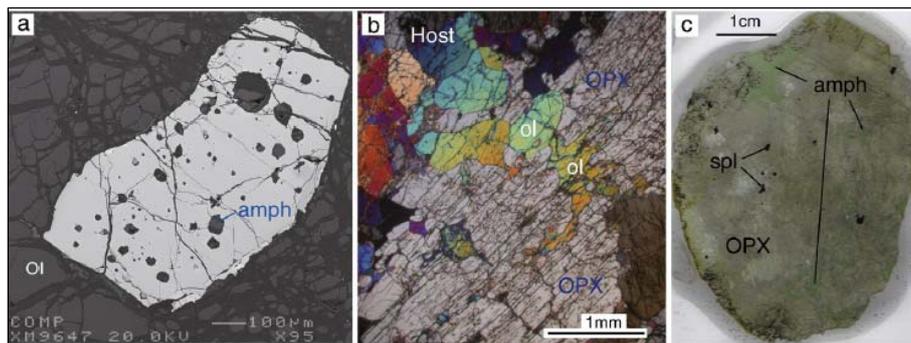
Fig. 3 - (a) Back-scattered electron image of a spinel grain with silicate mineral inclusions in harzburgites close to dunite. (b) Resorbed olivine in a large orthopyroxene grain in an orthopyroxenite. (c) Poikilitic amphibole (light green phase) in orthopyroxenite. amph = amphibole, ol = olivine, OPX = orthopyroxene, spl = spinel.

About 200 kilograms of chromite concentrate sand were collected in order to have a big amount of material for making new enrichment tests at the pilot plant of Omega Foundry Machinery LTD. in Peterborough (UK).

The portion of the concentrate sand from Krasta enrichment plant used for later enrichment tests has 48.51 wt.% Cr_2O_3 content and 9.09 wt.% SiO_2 content.

CHROMITE ORE CHEMICAL PARAMETERS FOR DIFFERENT MARKETS

Chromite is commercially used in three different market types, which require strict chemical and technical parameters (as shown in the Table 1). The refractory market is very limited due to the high chromite purity ($SiO_2 < 2.5$ wt.%) and therefore chromite sand assumes a high economic value. Nowadays the only country that produces chromite for refractories is South Africa thanks to its several stratiform chromite deposits with low SiO_2 content.

In this work, we focus on tests to reduce SiO_2 content of Krasta chromite concentrate sand by means of an innovative beneficiation technique.

Table 1 - Chemical and technical chromite parameters for three different market types. AFS-GFN = grain fineness number.

Market type	Cr2O3 (wt.%)	SiO2 (wt.%)	Ratio Cr/Fe	AFS-GFN	Melting point
Special steels	> 46	< 6	> 2	40 - 60	/
Ferro-chromium alloys	42 - 46	< 15	1.5 - 2	/	/
Refractories	> 38	< 2.5	/	40 - 60	> 2180 °C

AN INNOVATIVE BENEFICIATION TECHNIQUE (DM + IFS)

In order to meet the very demanding chemical parameter requirements for refractory market, chromite first concentrate sand, purified from fraction +1 mm and -150 µm grain sizes due to proper machineries working, was re-enriched using a combination of dry magnetic and gravity separation at the pilot plant of Omega Foundry Machinery LTD. in Peterborough (UK).

Re-enrichment was carried out using a Drum Magnet (DM) that works with a field intensity of 10,000 gauss. New concentrate was then processed by means of an Inclined Fluidised Separator (IFS) that works in dry conditions using an air cushion as fluidisation agent. IFS was designed for re-cycling of foundry sands and has not been applied yet to mine concentrates. Its high performance is due to the use of an air cushion as fluidizing agent that enhances the specific weight contrast between the grains in the sand.

ENRICHMENT TEST RESULTS: XRF ANALYSIS, GRAIN SIZE (AFS-GFN) AND XRPD ANALYSIS

At pilot plant in Peterborough (UK) a three steps enrichment test was performed:
- DM first step: Krasta feed was enriched using Drum Magnet and a concentrate (C DM) and a tail (T DM) were obtained;
- IFS second step: concentrate (C DM) was re-enriched using Inclined Fluidised Separator and a concentrate (C1 IFS) and a tail (T1 IFS) were obtained;
- IFS third step: tail (T1 IFS) was re-runned into Inclined Fluidised Separator and a concentrate (C2 IFS) and a tail (T2 IFS) were obtained.

XRF and grain size analysis, with grain fineness number (AFS-GFN) calculation, were carried out on each product achieved from enrichment test (as shown in Table 2).

The AFS Grain Fineness Number (AFS-GFN) is one means of measuring the grain fineness of a sand. GFN is a measure of the average size of the particles (or grains) in a sand sample. AFS-GFN gives the metal casting facility a means to verify its molding sand.

The grain fineness of sand was measured using a test called sieve analysis, which was performed as follows:

1. A representative sample of the sand was dried and weighed, then passed through a series of progressively finer sieves (screens) while they were agitated and tapped for a 15 minute test cycle.

2. The sand retained on each sieve (grains that are too large to pass through) was then weighed and recorded.

3. The weight retained on each sieve was divided by the total sample weight to arrive at the percent retained on each screen.

4. The percentage of sand retained was then multiplied by a factor, or multiplier, for each particular screen. (Table 1). The factors reflect the fact that the sand retained on a particular sieve (*e.g.* 50 mesh) is not all 50 mesh in size, but rather smaller than 40 mesh (*i.e.*, it passed through a 40 mesh screen) and larger than 50 mesh (it won't pass through 50 mesh screen).

5. The individual screen values were then added together to get the AFS-GFN of the sand, representing an average grain fineness.

Table 2 - XRF analyses (wt.%) of chromite from enrichment test at
Peterborough pilot plant and grain fineness number (AFS-GFN) of each product.

SAMPLES	FEED	C DM	T DM	C1 IFS	T1 IFS	C2 IFS	T2 IFS
Cr_2O_3	51.33	55.40	38.35	60.01	44.33	58.72	23.30
SiO_2	7.47	5.39	14.92	2.43	11.75	3.00	25.54
Al_2O_3	7.21	7.49	5.62	7.96	5.44	7.47	3.36
CaO	0.07	0.04	0.15	0.03	0.07	0.03	0.23
Fe_2O_3	14.08	14.95	10.63	15.61	12.32	14.01	7.31
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.16	0.17	0.13	0.17	0.16	0.16	0.11
MgO	19.22	17.14	25.91	14.38	22.81	14.91	34.78
Na_2O	0.22	0.23	0.16	0.26	0.17	0.23	0.06
P_2O_5	0.02	0.02	0.01	0.02	0.02	0.02	0.01
TiO_2	0.10	0.11	0.08	0.11	0.09	0.11	0.05
LOI	0.12	/	4.04	/	2.84	1.34	5.26
Total	100.00	100.94	100.00	100.98	100.00	100.00	100.00
RATIO Cr/Fe	3.57	3.62	3.53	3.76	3.52	4.10	3.12
AFS-GFN	66	56	78	42	83	41	88

These results highlight that C1 IFS is the best chromite concentrate obtained thanks to the first and second steps of the enrichment test, and it reaches chemical and technical parameters for refractory market (as shown in Fig 4 by blue triangle falling in R field) having Cr_2O_3 content of 60.01 wt.%, SiO_2 content of 2.43 wt.% and AFS-GFN of 42.

It is worth to notice that both C1 IFS and C2 IFS have a higher AFS-GFN than the feed. The increase in grain size of concentrate relative to feed is the opposite of what happens in shaking tables and is attained by the IFS thanks to its air cushion that favors flotation and hence discharge of finer grains. As usually concentrates from chromite beneficiation plants, like that of Krasta plant, are too fine for refractory market this property of IFS is pivotal for its use in production of refractory sands.

It is also important to observe that some other enrichment test products can be commercialized too. As a matter of fact concentrate C DM, extracted from drum magnet first step enrichment, falls inside special steels market field (pink triangle falling in SS field, Fig. 4) and has a suitable AFS-GFN (56). On the other hand concentrate C2 IFS, obtained from inclined fluidised separator third step enrichment, can certainly be used for special steel market and perhaps it can also be used for refractory market even if SiO_2 content is 3.00 wt.% (yellow triangle in Fig. 4).

Finally even the tail product of IFS second step enrichment test (T1 IFS) can be used for ferro-chromium alloy market (blue circle falling in A field, Fig. 4), although it has a high AFS-GFN of 83, which anyway is not an important parameter for this kind of product.
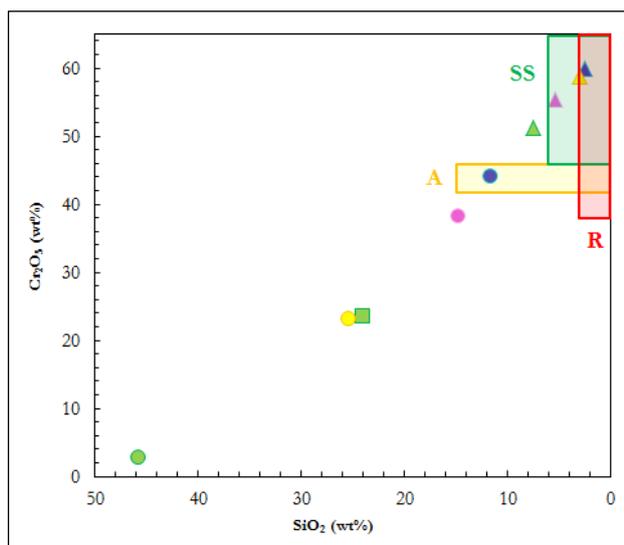
Fig.4 - Krasta chromite ore enrichment: products at Krasta plant (green symbols), DM first step (pink symbols), IFS second step (blue symbols) and IFS third step (yellow symbols) at Peterborough pilot plant. Square = feed, triangles = concentrates and circles = tailings. Green triangle is the feed of pink triangle, which is the feed of blue triangle, while blue circle is the feed of yellow triangle. Colored rectangles show the compositional fields of commercial chromite. A = ferro-chromium alloys, R = refractories and SS = special steels.

X-ray powder diffraction (XRPD) analyses were carried out on feed and on six different products obtained by three steps enrichment test in order to understand the mineralogical phases (chromite, olivine and serpentine) distribution into concentrates and wastes after magnetic and gravity enrichment.

Results show that drum magnet (DM) first step enrichment reports olivine to the tail (T DM) and chromite and serpentine to the concentrate (C DM), due to different magnetic susceptibility of mineralogical phases.

Instead chromite is separated from serpentine during inclined fluidised separator (IFS) second step enrichment because of its different density. In fact concentrate (C1 IFS) XRD pattern shows only chromite peaks while tail (T1 IFS) XRD pattern has a high intensity serpentine peak.

SEPARATION EFFICIENCY (SE) AND SIO$_2$ RECOVERY

At Peterborough (UK) Separation Efficiency (SE) was calculated for three steps enrichment test and total pilot plant using the equation proposed by Schulz (1970) and reviewed by Wills (1979):

$$SE = \frac{100Cm(c - f)}{(m - f)f}$$

where C is the fraction of the total feed weight that reports to the tail, m is the wt.% SiO$_2$ content of the gangue minerals, c is the SiO$_2$ wt.% of the tail and f is the SiO$_2$ wt.% of the feed.

Parameters for calculation of separation efficiency (SE) are shown in Table 3, where recovery values (C) refer for each step to its specific feed.

Table 3 - Separation Efficiency (SE) results of three steps chromite enrichment test and total plant SE.

Parameters	DM 1°step	IFS 2°step	IFS 3°step	Total
C	0.28	0.35	0.59	0.53
m (wt.%)	40.09	40.09	40.09	40.09
c (wt.%)	14.92	11.75	25.54	13.16
f (wt.%)	7.47	5.39	14.92	7.47
SE (%)	34.3	47.7	66.9	49.8

SiO$_2$ recovery is the fraction of silica in the feed that reports to the tail, while total SiO$_2$ recovery is the fraction of the total feed weight that reports to the tail and provides information on the amount of silica that can be removed from feed chromite sand (Table 4). The SiO$_2$ recovery increases during each step of enrichment test and it reaches the remarkable value of 92.5 wt.% in the inclined fluidised separator (IFS) third step.

Table 4 - Total recovery of concentrate (C) and tail (T) products and SiO$_2$ recovery results.

Test type	Samples	Partial recovery (wt.%)	Cumulate total recovery after 2° step (wt.%)	Cumulate total recovery after 3° step (wt.%)	SiO$_2$ recovery (wt.%)
DM 1° STEP	C DM	72	/	/	51.8
	T DM	28	28.0	28.0	
IFS 2° STEP	C1 IFS	65	46.8	46.8	72.3
	T1 IFS	35	25.2	/	
IFS 3° STEP	C2 IFS	41	/	10.3	92.5
	T2 IFS	59	/	14.9	
TOTAL TEST	CONC	57	/	/	83.2
	TAIL	43	/	/	

The best product is C1 IFS because further purification in the third step is attained at the expenses of a decrease in the recovery of concentrate as total recovery after each step is the product of the recoveries of all step performed. Purification processes like that performed in this test are characterized by low SE values due to the necessity to maintain high total recoveries. Separation efficiency for the Peterborough pilot plant of 49.8 % can be considered very good for a product that has already undergone an intensive enrichment treatment like that performed at Krasta plant. IFS second step provides a high quality concentrate for refractory market at a relatively high cumulate recovery of 46.8 wt.% (Table 4). Moreover, T1 IFS at a cumulate recovery of 25.2 wt.% is a product that can be used for the iron-chromium alloy market and only 28 wt.% of the feed is discharged. IFS third step adds, with C2 IFS, 10.3 wt.% more product that could be useful for the refractory market while T2 IFS is added to the discharge. In total performing all three steps we can get a 57.1 wt.% of excellent concentrate for

refractory market and 42.9 wt.% discharge. An economic analysis of costs and market values can discriminate between this option and the alternative option of performing only first and second steps.

CONCLUSIONS

Refractory chromite sand chemical and technical requirements are very demanding and no chromite ore can attain them by simple crushing. On the other hand usual enrichment methodologies either cannot meet the required parameters or have a very low refractory sand recovery.

The combination of Drum Magnet (DM) and Inclined Fluidised Separator (IFS) in the Omega Foundry Machinery LTD. pilot plant not only produces a good quality refractory sand, but the result is reached with an high recovery, making of this plant an optimal solution for the production of refractory chromite sand.

The Inclined Fluidised Separator is particularly performing as it combines a very high recovery of silica in the tail with an increase of the grain size of concentrate.

Albanian chromite ore is suitable for production of refractory sand with the new beneficiation technique and it has two more minor benefits: the high olivine/serpentine ratio in the gangue and the high Cr_2O_3 content of chromite.

The high Cr_2O_3 content of Albanian ore chromite allows also the use of part of the tailings produced for the iron-chromium alloys and the special steels industries.

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