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EAF SLAG TREATMENT FOR INERT MATERIALS PRODUCTION

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Introduction

Recently, those countries which are more concerned with the environmental protection (Europe, USA, ...), are following two main routes for handling steel mill byproducts:

- development and application of innovative and more efficient technologies to decrease liquid, solid and gaseous emissions;
- valorization of the *waste materials* (according with the Zero Waste Philosophy) both for the recovery of the valuable fractions (e.g. ZnO from the EAF dust) and to enhance, after treatments, the material properties for their reuse as building materials.

These virtuous routes lead, as a positive effect, to the increase of knowledge at the microstructural level of the materials, and to the development of plants more efficient in turning waste materials into inert ones, being equivalent for their chemical-physical properties to natural substances used in constructions.
The project, developed by Danieli in collaboration with Politecnico di Milano, allowed to reproduce experimentally the philosophy described above on the Electric Arc Furnace (EAF) slag, in order to solve some issues linked to: metals (as Cr, V, Ba, …) leaching[1,2], free lime concentration decrease[3], production of materials with mechanical properties suitable for building purposes[4]. Project steps have been:

- steel-plant slag microstructural analysis and leaching behavior characterization;
- laboratory test: investigations on inertizing additives and effects on phases transformation;
- optimal process conditions definition for industrial scaling up;
- pilot plant design and construction to test the inertization technologies into steel-plant;
- tests in steelmaking plant and industrial technology validation.

Experimental procedure

Experimental tests have been split into two steps: laboratory and pilot plant testing in steelmaking plant.

Lab testing

Different slags samples have been selected from various steel-plants, with a Cr, Ba and V content potentially at elution risk. After the chemical and physical characterization and the measurement of metallic ions concentration during leaching test, slag samples have been subjected to inertization trials, by melting them into a resistive furnace (T_{max} = 1400 °C), using a ceramic crucible, and adding oxides mixtures such as SiO_2, FeO and MgO. In Table 1 the conditions experimentally investigated are reported.

Table 1: Composition of the additive for the liquid slag inertization in the lab scale

Sample	Oxides mixture	Cooling medium	Results
1	Mainly SiO_2	Natural convection	Optimum
2	Mainly MgO		Partial
3	Mainly FeO		Partial

Pilot plant testing

The plant consists of a silo stocking the oxide mix and a metering valve supplying and conveying it through the pneumatic transport to a nozzle, lying close to the EAF slagging door.

Great efforts have been devoted in studying and developing the injection plant: process parameters, such as transport air pressures, rates, injection nozzle position and shape, have been designed in order to improve the mixing of the slag with the inertizing flux, aim to enhance the reaction of transformation of water-soluble phases (such as larnite, brownmillerite) into stable ones, such as wustite and Cr-Mg spinel. A suitable control system guarantees the accurate injection timing, while optimizing the mixture consumption.

A summary of the applied conditions is reported in Table 2.

Table 2: Experimental parameters for the pilot plant testing

Parameters	Value
Air flow rate [Nm^3/h]	150 ÷300
Dispenser internal pressure [bar]	2 ÷4
Air pressure [bar]	0 ÷ 3.5
Additive flow [kg/min]	0 ÷ 140

Chemical and physical characterization

Both samples, the one prepared in laboratory and the other coming from the steel-plant, have been characterized with these techniques:

- XRF, to evaluate the average chemical composition;
- SEM-EDS, to analyze the morphology and composition of the slag phases;
- leaching test, in agreement with UNI EN 12457-2/04;
- free CaO concentration analysis, in agreement with UNI EN 17441:2013;
- Los Angeles coefficient determination, in agreement with UNI EN 1097-2.

Results and discussion

Lab results

Laboratory test performed by Politecnico di Milano allowed studying different inertizing additives formulations. As cast and treated slag have been compared each other, taking into account existing phases and metallic ions leaching.

In Figure 1a comparison between as-cast slag (on the left) and laboratory re-melted with high SiO_2 addition (on the right) is reported.

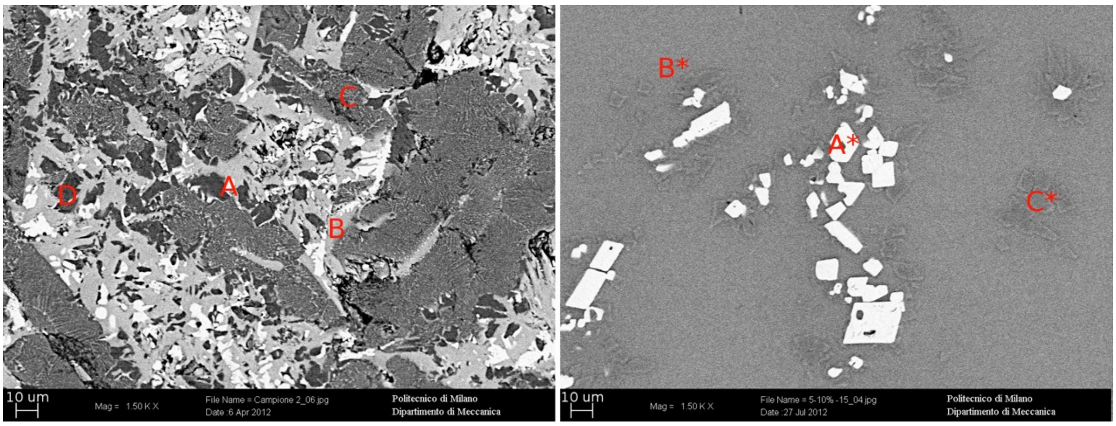

Figure 1: SEM images of as cast slag (left) and produced in lab scale (right)

The as-cast slag consists of four main phases: magnesium-wustite (phase A), brownmillerite (phase B), hatrurite C_3S (phase C) and larnite C_2S (phase D).
Calcium-silicates (C_3S, C_2S) own well known hydraulic properties and the high content of heavy metals dissolved within, identify them as potential responsible for Ba and V leaching (Table 3).[5] Brownmillerite, also, belong to the main constituents of the cement and possess modest hydraulic properties that could heighten the leaching of Ba and Cr dissolved within (Table 3).[6,7]

Table 3: Oxides partitions in the different phases (Lab scale – as-cast slag)

Phase	Symbol	Cr_2O_3	BaO	V_2O_5	TiO_2
Mg-Wustite	A	0.5 %	4.0 %	6.5 %	0.0 %
Brownmillerite	B	99.0 %	48.0 %	32.0 %	100.0 %
Hatrurite	C	0.5 %	20.0 %	16.5 %	0.0 %
Larnite	D	0.0 %	28.0 %	45.0 %	0.0 %

Through the addition of inertizing mix oxides, phase transformations occur and the slag obtains a structure similar to the one on the right in Figure 1. The slag microstructure is formed by a Si-rich glassy matrix (B*), where silicate crystals characterized by high content of MgO, Al_2O_3 and FeO (C*) and Cr-rich spinels (A*) nucleate. The addition, preferably quartzite, seems to promote the unmixing of chromium that tends to bind with Mg-wustite forming stable Mg-Cr-spinels, which also act as the nuclei where the silicate crystals start to nucleate and grow. These structures are stable[8], and, as a consequence, Cr can be considered to be irreversibly sequestered.

Table 4: Oxides partitions in the different phases (Lab scale - treated slag)

Phase	Symbol	Cr_2O_3	BaO	V_2O_5	TiO_2
Cr-Mg Spinels	A	99.0 %	50.0 %	35.0 %	0.0 %
Glass	B	0.4 %	32.0 %	50.0 %	36.0 %
Pseudowollastonite	C	0.6 %	18.0 %	15.0 %	64.0 %

Even if the addition takes place at solid state, the silica effect on the slag melting temperature is enough to promote the liquefaction of the solid mass. Nevertheless the added inertizing mix completely dissolves in the slag and SEM analysis does not pointed out unmixed SiO_2 or other additive particles. SiO_2 enrichment converts C_3S and C_2S into Pseudowollastonite (CS), and the formation of liquid eutectic compound contributes to envelop the new crystalline phases into a glassy matrix, unreactive with water, and, accordingly, Ba, V and Cr leaching have been effectively avoided (Table 5).

Table 5: leaching tests: limit concentrations and lab results on as-cast and treated slag

Species	Limit concentrations [mg/L][1,2]	As cast slag [mg/L]	Treated slag [mg/L]
Ba	1.0	**2.31**	0.11
Cr	0.05	**0.7**	0.035
V	0.25	< 0.001	< 0.001
pH	5,5 <> 12	**12.2**	10.0

Pilot plant results

Pilot scale validation of laboratory investigation have been realized through pneumatic transport in air of the oxides mix from a storage silo to a nozzle, placed in such a way to allow an optimal liquid slag - additives mixing, to maximize the effects of stabilization.Results obtained in pilot scale have been very positive, as an inertized slag SEM images demonstrates (Figure 2).

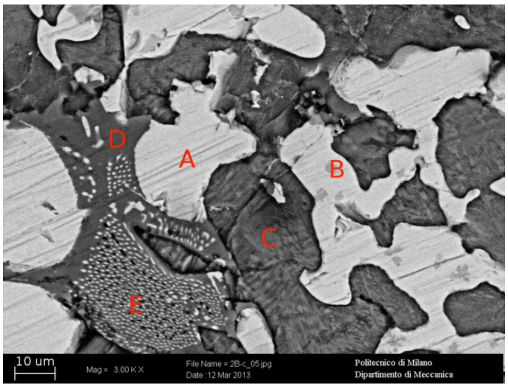

Figure 2. SEM image of treated slag produced during pilot plant trials

The experimental evidence demonstrates that silica is able to react with slag. The decrease in C_3S and the free CaO fraction is a glaring evidence that silica dissolves and reacts with the molten slag, even if larnite (phase C) residual is still visible. The increase in wustite (phase A) fraction and the formation of Cr-Mg spinels (phase B) and gehlenite (phases D, E) are also unequivocal indexes that quartzite positively modify the slag microstructure. As reported in Table 6, oxides subjected to elution have been incorporated in stable structures (Cr-Mg spinels and gehlenite[9]), also

reducing those dissolved in larnite. Leaching tests results (Table 7) confirm the occurred inertization.

Table 6: Oxides partitions in the different phases (pilot plant scale- treated slag)

Phase	Symbol	Cr_2O_3	BaO	V_2O_5	TiO_2
Mg-Wustite	A	8.0 %	8.0 %	3.0 %	0.0 %
Spinelli Cr-Mg	B	89.0 %	15.0 %	92.0 %	100.0 %
Larnite	C	0.0 %	26.0 %	0.0 %	0.0 %
Gehlenite	D, E	3.0 %	51.0 %	5.0 %	0.0 %

Table 7: Elution tests: limit concentrations and result for the slag produced by the pilot plant

Metals	Limit concentrations [mg/L][1,2]	As cast slag [mg/L]	Treated slag [mg/L]
Ba	1.0	**2.31**	0.20
Cr	0.05	**0.7**	0.033
V	0.25	< 0.001	0.073
pH	5,5 <> 12	**12.2**	11.7

Finally, mechanical tests performed on both as-cast and pilot-plant treated samples demonstrated that the inertization process preserves slag properties: treated slag Los Angeles coefficient LA is similar to the one of as-cast slag (LA<30) (Table 8). Slag with this characteristic could be exploited for concrete pavers or bituminous binder layers, in addition to all the base and foundation layers applied in the road constructions.

Table 8: Los Angeles values comparison between as-cast and inertized slag

Sample	**L.A.**
As-received fresh	28
As-received aged	25
Inertized 1	25
Inertized 2	27

Conclusions

EAF slag inertization process and plant, characterized by pneumatically conveying the inertizing oxide mix into the molten slag, developed by Danieli in collaboration with

Politecnico di Milano, promotes stable phases formation, able to retain metallic ions leaching over prescribed limits and maintaining the same mechanical properties of the as-cast slag.
This expands EAF slag uses, as an aggregate in civil engineering, utilization so far forbidden because of heavy metals leaching over limits.
Simple plant implementation and easy process operation are two key points of this technology.

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