# **RESEARCH ARTICLE**

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# The Use of Secondary Metallurgy Slag as Soil Corrective in Agriculture: Approval of Their Application in Italy

Davide Mombelli,\* Gianluca Dall'Osto, Sara Scolari, Carlo Mapelli, Roberto Moreschi, Roberto Marras, and Riccardo Morandi

Among the steelmaking slag, secondary metallurgy slag (SMS) is the most problematic to be recycled. Several attempts to recover such slag as lime replacement, slag flux, pozzolanic materials have been made for long time with pros and cons. However, the amount of recyclable slag is limited and often their employment requires higher energy demand than traditional materials. Nevertheless, the use of SMS in agriculture is poorly or never considered. In this article, the legal and technical evaluation of SMS as raw material for fertilizers production is investigated. Compliance of technical specification, toxic metals concentration, and leaching behavior allows to confirm the technical feasibility of SMS use as a raw material for fertilizers manufacture. Both from the literature data and the experimental results on 16 industrial SMS samples, the requirements for calcium-magnesium-sulfur-based fertilizers, soil correctives and for sanitizing agricultural sewage sludge, appear fully satisfied. The CaO concentration in SMS (35-60 wt%) is abundantly higher than the requirements (≥15 wt%) and CaO is present in most part as water-soluble complexes such as calcium aluminates (70 wt%), silicates (10 wt%), and sulfide (4 wt%). The pH of the SMS samples leachate is comparable to that of fresh lime (12.35 vs 12.46), highlighting a better behavior for sewage sludge sanitation with respect to limestone (9.98). The measured toxic metals and leachate elements concentration over the corresponding admittable threshold are always lower than 0.5 and 1.0 (mg kg<sup>-1</sup>/mg kg<sup>-1</sup>) for liming materials. Finally, these results lead to officially approve the use of SMS as soil corrective according to the Italian Fertilizer Regulation.

#### high environmental and energetic impact with a high consumption of minerals and carbon coke in addition to the generation of significant amounts of solid waste.<sup>[1]</sup>

Still, to meet the growing demand for quality steels, from the mid-1960s the secondary steelmaking treatments and plants were developed as a complement to the refining of steel in the melting furnace. Secondary steel refining homogenizes the temperature and composition of the steel bath; facilitates decarburization, desulfurization, deoxidation, nitrogen and hydrogen removal, and attainment of the required teeming temperature; controls the shape of the inclusions; and improves the cleanliness of the steel.<sup>[2]</sup> Over the years, the continuous increase of steel production by electric arc furnace (EAF), at the expense of the blast furnace-basic oxygen furnace (BF-BOF) route, led to a widespread diffusion of the secondary steel refining also for less qualified steels, and nowadays about 70% of produced steels undergo at least one refining treatment. Given the wide range of possibilities and specific needs of each steelmaking plant several secondary metallurgy processes have then emerged, like ladle furnace treatment (LF), vacuum degassing (VD), argon oxygen decarburization

# 1. Introduction

Steel production is one of the most ancient activities in human history. Iron and its alloys have formed the basis of scientific and technological progress of humankind. Despite the will for the sector's decarbonization, steelmaking is inherently bound to a

D. Mombelli, G. Dall'Osto, S. Scolari, C. Mapelli Dipartimento di Meccanica Politecnico di Milano Via La Masa 1, 20156 Milano, Italy E-mail: davide.mombelli@polimi.it

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R. Moreschi

Accieria Arvedi S.p.A. via Acquaviva 18, 26100 Cremona, Italy

R. Marras Formerly Unicalce S.p.A. via Ponti 18, 24012 Val Brembilla (BG), Italy

(AOD), and vacuum oxygen decarburization (VOD).

On the contrary, each of the steelmaking related processes has

as one of the main outputs the generation of significative amount

of slag, sludge, and dust. For example, BF-BOF route produces

 $\approx$ 200–250 kg of slag (BOFS) per tonne of produced steel.<sup>[3]</sup>

R. Morandi Unicalce S.p.A. via Ponti 18, 24012 Val Brembilla (BG), Italy Similarly, steel production by EAF is accompanied by about 100 kg of slag (EAFS) per tonne of steel produced, commonly referred to as black slag due to the high fraction of iron oxide that gives the distinctive black color. Furthermore, smaller quantities of other wastes like dust, secondary metallurgy slag (2.5%), and refractories are generated during the electric steel production.

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On the one hand, EAFS and BOFS have slowly carved out a space for themselves in the waste-to-value trade as a suitable technical alternative to natural stones for several engineering applications. On the other, the recovery of refining slag or secondary metallurgy slag (SMS), commonly referred to as white slag due to the distinctive color given by the high fraction of lime, is currently very limited, although accounting for 14% of the whole amount of European steelmaking produced slag, that is, based on the most recent data found, roughly 3 Mt in 2021.<sup>[4–6]</sup>

Nevertheless, several attempts at sustainable recycling of ladle refining slag are reported in literature. For example, different approaches have been pursued to avoid the volume expansion and self-dusting phenomena that inhibit their use as crystalline aggregates for concrete or road construction. On this regard, a common way already adopted for BOFS and EAFS stabilization,<sup>[7,8]</sup> is the addition of slag stabilizers during the tapping like B-, P-, and SiO<sub>2</sub>-based compounds (Dehybore, Vitribore, PV1) or Al<sub>2</sub>O<sub>3</sub>-based compounds (Valoxy).<sup>[9–13]</sup> The goal of these stabilizers is to transform or prevent the dicalcium silicate volumetric expansion ( $\beta \rightarrow \gamma$ ).<sup>[14–16]</sup> In a similar way, fast cooling of SMS was also proposed to freeze dicalcium silicate in  $\gamma$ -form without the intermediate formation of  $\beta$ -form.<sup>[10,17]</sup>

As an alternative to landfill disposal, SMS can be recirculated as a replacement of fresh lime into the previous step of the steelmaking process (converter or electric arc furnace melting) or in the ladle itself.<sup>[10,18-20]</sup> Industrial tests have demonstrated the feasibility of refining slag recirculation, but the amount of recovered slag is limited, and the energy consumption of the process tends to increase. For example, in the face of a load of 1 tonne of LF slag into a 130 tonnes Linz-Donawitz (LD) oxygen converter, a saving of 3.5 kg of fresh lime per tonne of hot metal was achieved but the blowing time increased by 4% as well as the FeO concentration and the volume of the slag.<sup>[18]</sup> Similarly, the recirculation of LF slag into the ladle offers limited advantages: only 2-5 tonnes of slag can be recycled because every re-charge requires a further addition of fresh lime to maintain the same desulfurization capacity and the volume of slag continuously increases, thus making more than three consecutive cycles impossible.<sup>[19]</sup>

In some cases, SMS was used as fluxes being formed by calciumaluminate which is the main component of ladle fluxes.<sup>[21,22]</sup> These fluxes are widely used in clean steel production processes. Hence, using ladle furnace slag as a part of ladle fluxes can be considered as an economic recovery for these materials. Industrial trial results have shown that the ladle slag can be used up to 75 wt% in synthetic flux without adversely affecting the steel chemistry. This entailed a reduction of 600 kg lime per heat and 0.1 kg t<sup>-1</sup> of aluminum.<sup>[21]</sup>

A more promising use is its adoption in the formulation of construction material mixtures, exploiting its pozzolanic properties and hydraulicity. Masonry mortars are typical products where the SMS can effectively replace both fillers and binders, without any depletion of mechanical strength, workability, and water retentivity.<sup>[23–25]</sup> Otherwise, SMS can be again employed as a substitute of fillers and fine aggregates during the manufacturing of porous asphalt mix without altering the main physical properties of the asphalt, <sup>[26–28]</sup> or as a lime alternative to unpaved road stabilization, <sup>[29]</sup> or as a self-sealing layer for landfilling insulation. <sup>[30]</sup> Finally, slag can also be exploited as artificial aggregates in conglomerates after their granulation. It should be noted, however, that although wet granulation is preferred for the treatment of ironworks slag, SMS slag is commonly treated with dry granulation to avoid the potential evolution of H<sub>2</sub>S.<sup>[31–33]</sup>

However, an evaluation of a potential use of SMS in agriculture was never considered, as instead was done for other kind of steelmaking slag. For example, the use of Thomas converter slag as a raw material for phosphate fertilizers began to spread mainly in Europe at the end of the 19th century but has decreased sharply since the mid-1970s as the NPK (nitrogen-phosphoruspotassium) chemical fertilizers started to be used. Thomas phosphate fertilizer has been partially replaced by modern LD converter slag as a P-source for plant growth. However, LD converter slag have a limited concentration of P (<1.5 wt%) and currently it is mainly used as a liming product only, especially for forest liming.<sup>[34]</sup> Nonetheless, recent field trials confirmed an increase in the growth of legumes when commercial fertilizer was substituted with LD converter slag.<sup>[35]</sup> Silicate fertilizers, made by blast furnace slag, are currently in use both in Japan and U.S., under specific regulations.<sup>[36]</sup> Furthermore, liming materials made by iron- and steel-making slag (blast, converter, and ladle furnaces) were included in the EN 14 069 standard, but unfortunately they are not linked with any EU regulation although their technical effectiveness in neutralizing soil acidity has been proved.[37-39] The major limit to the use of oxidized slag (i.e., BOFS and EAFS) is the high risk of toxic metals leaching,<sup>[40,41]</sup> like Cr, Ni, Cd, V, that obliged to add strict limitations about hazardous constituents in the regulations. In this regard, even if the harmlessness and biological efficiency of BOFS amendment in rice crop fields has been very convincingly evaluated by Das et al.<sup>[42]</sup> which highlighted a positive impact on the soil nutrient availability and plant uptake with an overall improvement of the crop yield, the risk of soil overliming and subsequent animal intoxication must be seriously considered due to currently limited and inconclusive evidence on the long-term effects of slag fertilizer application to soil.<sup>[37,43]</sup> On the contrary, being the SMS mainly formed by CaO-rich compounds and given the reducing conditions of steel refining in the ladle, such slag may be safely employed as lime-based fertilizers without any risk of toxic metals leaching.

In this article, the legal and technical feasibility of SMS exploitation as a raw material for fertilizer production will be discussed. Based on the examination of the current regulatory framework and the chemical properties of slag from secondary metallurgy, the various possibilities of using SMS as a fertilizer or soil conditioner will be presented and discussed. Although there are several attempts to demonstrate the liming and fertilizer capacity of steel slag, at a legal framework level there were no allowances, at least in Italy, for the recovery of refining steelmaking slag as soil fertilizer prior to the conceptualization of this work. Thus, the novel aim of this work is to prove the compliance of SMS with the requirements for the approval and registration of new agricultural products (fertilizer, corrective, sanitizer). Specifically, in order to provide tangible evidence of these applications, the experimental results obtained from a series of 16 SMS samples were compared with the thresholds imposed by the legislations. The successful approval of ladle furnace slag as soil corrective obtained by Italian Agriculture Ministry validates the methodology adopted, which can be replicated in the future to obtain additional approvals also at European framework.

### 2. Regulatory Framework

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#### 2.1. Fertilizers

The regulations and legislative decrees currently in force, both at Italian and European community level, do not indicate any suitability or prohibition of using a steelmaking by-product as a raw material for fertilizers production. An exception is the already mentioned Thomas converter phosphate slag (classified as EC "A.2.1" fertilizer and suitable for organic agriculture), which today appears to be an obsolete process with no more working stations.

Fertilizers marketed in the European community must comply with the European regulation EC 2003/2003 and are the only that can bear the CE mark.<sup>[44]</sup> A manufacturer can propose the inclusion of a new type of fertilizer and for this purpose a specific procedure must be followed. A fertilizing products regulation (FPR) has been approved and has been in force since June 2021 (EU 2019/1009), with its application starting from 16th July 2022, coinciding with the expiration of EC Regulation 2003/2003.<sup>[45,46]</sup> This new regulation contains specifications for components (CMC) and products functionalities (PFC). A specific article for EU fertilizing product containing by-products within the meaning of Directive 2008/98/EC (CMC 11) has been enacted. This framework establishes for each fertilizer category (organic, inorganic, mineral, corrective, etc.) the threshold values for macroand micro-elements and the maximum admitted concentration of toxic metals.

In an attempt to better regulate the criteria for the industrial by-products application in fertilizers, a delegated act (EU 2022/973) was adopted on 14<sup>th</sup> March 2022.<sup>[47]</sup> Furthermore, at the recommendation of the Joint Research Center, ferrous slag was specifically mentioned, along with additional limiting concentrations of elements contained in the by-products.<sup>[46]</sup>

The limits of toxic metals and compounds given in the above regulations for inorganic fertilizers based on macro-elements are given in **Table 1**.

Beside the Community legislation, every country can adopt a national legislation on fertilizers. In Italy, fertilizers are regulated by the Legislative Decree 75/2010 (D.Lgs. 75/2010) that extends the European list of usable fertilizers with a national one.<sup>[48]</sup>

As reported in the Chapter 7 of the aforementioned legislation, the SMS may respond to all the requirements for "calcium-magnesium-sulfur-based fertilizers" manufacturing. Such fertilizer requires at least  $a \ge 15$  wt% water-soluble CaO, 8/10 of which in the form of a complex. In addition, the presence and declaration of micro-elements are also guaranteed, if they respect the threshold values reported in Chapter 1 of the aforementioned decree (Table 2). Alternatively, only for national fertilizers listed in Annex 1 – Chapter 2 to 6, the SMS might be used to add both secondary (meso-) and micro-elements or only secondary elements to fertilizers listed in Chapter 8. The secondary

**Table 1.** Maximum admitted concentration of toxic metals (mg kg<sup>-1</sup> on dry matter – dm –) and compounds in inorganic fertilizers based on macro-elements (referred to the EU regulation).<sup>[45,47]</sup>

Element/compound	Unit	Threshold
EU 2019/1009 <sup>[45]</sup>		
Cadmium (Cd)	$ m mgkg^{-1}dm$	$\leq$ 3
Hexavalent chromium (Cr(VI))	$ m mgkg^{-1}dm$	≤2
Mercury (Hg)	$ m mgkg^{-1}dm$	≤1
Nickel (Ni)	$ m mgkg^{-1}dm$	≤100
Lead (Pb)	$ m mgkg^{-1}dm$	≤120
Arsenic (As)	$ m mgkg^{-1}dm$	≤40
Copper (Cu)	$ m mgkg^{-1}dm$	$\leq$ 600
Zinc (Zn)	$ m mgkg^{-1}dm$	≤1500
Biuret ( $C_2H_5N_3O_2$ )	$ m mgkg^{-1}dm$	≤12
Perchlorate ( $ClO_4^-$ )	$ m mgkg^{-1}dm$	$\leq$ 50
EU 2022/973 <sup>[47]</sup>		
Total chromium (Cr <sub>TOT</sub> )	$ m mgkg^{-1}dm$	$\leq$ 400
Thallium (Tl)	$ m mgkg^{-1}dm$	≤2
Vanadium (V)	$ m mgkg^{-1}dm$	$\leq$ 600

elements envisaged by the decree are CaO, MgO,  $Na_2O$ , and S, whose thresholds are still indicated in Chapter 1 (Table 2).

#### 2.2. Correctives

A further option can be the qualification of SMS as a corrective (liming material), that is, a material added in situ to modify or improve some anomalous chemical properties of a soil depending on reaction, salinity and sodium content. The characteristics of Italian correctives are reported in the Annex 3 of D.Lgs. 75/2010. Calcium–magnesium–sulfur–based correctives are classified according to granulometry as:

Powder product:  $\geq$ 80 wt% of the product must have a particle size <0.3 mm and 100 wt% of the product must have a particle size <1 mm;

Shred product:  $\geq$ 80 wt% of the product must have a particle size <5 mm;

Crude product  ${<}80\,{\rm wt\%}$  of the product must have a particle size  ${<}5\,{\rm mm};$ 

Granular product: artificially granulated product whose particle size must be declared by the manufacturer (e.g.:  $\geq$ 80 wt% of the product with particle size <X mm; 100 wt% of the product with particle size <Y mm).

In order to be used as a corrective, the material must respect concentration limits on several toxic metals (**Table 3**). The same limitations are also imposed to soil improvers, even if there are no specific inorganic compounds on the eligible list. On the contrary, the new EU 2019/1009<sup>[45]</sup> includes both specifications for correctives (liming material – PFC 2) and inorganic soil improvers (PCF 3(B)) as well as adds specific threshold limits on the maximum admitted toxic metals (Table 3). It is interesting to observe that the EU limits are less restrictive than the Italian ones, except for lead, nickel, and arsenic (only for inorganic soil improvers).

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Element	Parameter to be declared	Meso-elements threshold	Mic	ro-elements threshold	
			Full field or pastures	Vegetable	Nebulizatior
Ca	CaO soluble in $H_2O$	$\geq$ 2 wt%	_	-	-
	CaO Total	≥8 wt%			
Mg	MgO	$\geq$ 2 wt%	-	-	-
S	SO <sub>3</sub>	$\geq$ 5 wt%	-	-	-
	S	$\geq$ 2 wt%			
Na	Na <sub>2</sub> O	$\geq$ 3 wt%	-	-	-
В	В	-	≥0.01 wt%	≥0.01 wt%	≥0.01 wt%
Co	Co	-	$\geq$ 0.002 wt%	-	$\geq$ 0.002 wt%
Cu	Cu	-	≥0.01 wt%	$\geq$ 0.002 wt%	$\geq$ 0.002 wt%
Fe	Fe	-	$\geq$ 0.5 wt%	$\geq$ 0.02 wt%	$\geq$ 0.02 wt%
Mn	Mn	-	$\geq$ 0.1 wt%	$\geq$ 0.01 wt%	$\geq$ 0.01 wt%
Мо	Мо	-	≥0.001 wt%	$\geq$ 0.001 wt%	$\geq$ 0.001 wt%
Zn	Zn	_	≥0.01 wt%	>0.002 wt%	≥0.002 wt%

Table 3. Maximum admitted concentration of toxic metals in corrective (liming material) and soil improver (referred to Italian and EU regulations).

Element	Unit	Corrective threshold	ls (liming material)	Soil improver thresholds			
		D.Lgs. 75/2010 <sup>[48]</sup>	EU 2019/1009 <sup>[45]</sup>	D.Lgs. 75/2010 <sup>[48]</sup>	EU 2019/1009 <sup>[45]</sup>		
РЬ	$ m mgkg^{-1}dm$	≤140	≤120	≤140	≤120		
Cd	$ m mgkg^{-1}dm$	≤1.5	$\leq$ 2	≤1.5	≤1.5		
Ni	$ m mgkg^{-1}dm$	≤100	$\leq$ 90	≤100	≤100		
Zn	$ m mgkg^{-1}dm$	$\leq$ 500	$\leq$ 800	$\leq$ 500	≤800		
Cu	$ m mgkg^{-1}dm$	≤230	$\leq$ 300	≤230	$\leq$ 300		
Hg	$ m mgkg^{-1}dm$	≤1.5	≤1	≤1.5	≤1		
Cr (VI)	$ m mgkg^{-1}dm$	≤0.5	$\leq$ 2	≤0.5	≤2		
As (inorganic)	$ m mgkg^{-1}dm$	-	-	-	≤40		

#### 2.3. Chemical Stabilizers and Sanitizers for Sewage Sludge

2.4. EoW

A further opportunity to profitably reuse the refining slag is replacing lime in the treatment of sewage sludge. This practice is regulated by the Legislative Decree 99/92 (D.Lgs. 99/92).<sup>[49]</sup> Sewage sludge treatment aimed at reducing the fermentation activity and health risks and it must be applied before its use in agriculture, as stated in art. 2, paragraph 3.b and art. 3 of the aforementioned decree. The recovery of sewage sludge for agricultural uses is authorized pursuant to the Ministerial Decree 05/02/98 (D.M. 05/02/98).<sup>[50]</sup> One of the processing operations provided by both the D.Lgs. 99/92 and Lombardy Region Resolution, Annex 4<sup>[51]</sup> consists in the sludge stabilization with lime to bring the pH of the treated mass to 12 for a specific period. Lime can be replaced with a lime-based product having the same sanitizing effect. The stabilized mass must then comply with some limitations, that is, toxic metals concentration, dioxins, and bacteria (Table 4).

To effectively exploit secondary steelmaking slag for agricultural application, the End-of-Waste (EoW) procedure must be fulfilled. This implies the actuation of such a procedure for which a waste, subjected to a recovery process, loses its definition to acquire that of a product. A waste ceases to be such when it has been subjected to a recovery operation and satisfies all the conditions established by art. 6 of the framework directive, as amended by the European Directive 2018/851/EU.<sup>[52]</sup> This has been implemented in the Italian Legislative Decree 15/2006 (D.Lgs. 152/ 2006).<sup>[53]</sup> The recovery operation may simply consist in an inspection to verify if a waste meets the criteria aimed at defining the EoW. These criteria are adopted in accordance with what is established by the community discipline or, in the absence of community criteria, case by case for specific types of waste through one or more decrees of the Environment Ministry. Such criteria may include limit values for pollutants and consider

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Unit Threshold D.Lgs. 99/92 Threshold D.G.R. X/2031 Parameter Compliant sludge High quality sludge 5 5-11 pН \_ \_ 5.5-11 Dry mass @ 105 °C % \_ Dry mass @ 600 °C % VSS/TSS % < 60 < 65  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ Toxic metals As <10  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ Cd <20 <5 <20  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ Cr tot \_ <150 <750  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ <400 Cu <1000 <1000  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ Hg <10 <5 <10  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ <300 Ni <300 <50 Ph  $mg kg^{-1} dm$ <250 <750 <750  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ 7n <2500 <600 <2500 C organic >20 >20 Agronomic parameters Ν % dm >1.5 >1.5 P % dm >0.4>0.4к % dm Moisture DH%  ${
m mg}\,{
m kg}^{-1}\,{
m dm}$ Organic pollutants РАН < 6 PCB  $mg kg^{-1} dm$ < 0.8 PCDD/F ng TEQ/kg dm < 50 Micro-biological parameters Salmonella MPN/g dm <1000 <100 Faecal coliforms MPN/g dm <10 000

Table 4. Threshold values for high quality stabilized sludge and compliant stabilized sludge agriculture use (referred to the Italian regulation).<sup>[49]</sup>

all possible negative effects on the environment. Pending the adoption of one or more specific decrees, waste recovery must fulfill the requirements stated in some decrees currently in force. For steelmaking slag, simplified recovery procedures for bulk granulated slag are still regulated by D.M. 05/02/98 which recommends compliance with the threshold concentrations in the leachate of some elements.

Phytotoxicity

#### 2.5. REACH Registration

**Biological parameters** 

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For each new product entered the market in quantities equal to or greater than 1 tonne, the compliance with the REACH and CLP regulations must be assessed. Fortunately, the procedure for secondary metallurgy slag registration is simplified, because this slag has been already assigned to an EINECS (266-004-1) and CAS (65 996-71-26) numbers. Thus, each registrant has only to demonstrate that the substance he intends to register meets the sameness criteria given in the Lead Registrant's dossier. To prove the sameness of secondary steelmaking slag, production process, mineral components, chemical composition, and position of the chemical composition within a given composition diagram must be checked (**Figure 1**).

# 3. Secondary Metallurgy Slag Properties

Secondary metallurgy slag represents a wide family of slag, originating from different processes, typically having high CaO content, low levels of oxidation, and being saturated with MgO (**Table 5**).

Growing Test (Annex B D.G.R. 16/04/2003 n. 7/12 764) or germination (dilution 30%) >60%

Although most of the secondary metallurgy slag have a concentration of FeO +  $MnO + Cr_2O_3$  less than 1 wt% to properly deoxidize the steel, higher concentration of such oxides sometimes occurs. Typically, this oxidized refining slag are associated to those processes where slag carry-over is useful to produce a ready-melt slag or recover some valuable compounds, like Cr in AOD conversion, but this represents more of an exception.

Although, traces of other metals due to some ferroalloy losses (B, Mo, Co, etc.) are expected to be present in the SMS, during their typical characterization these elements, given low concentration (on the order of ppm), are not taken into account and therefore they are not reported in the authors known literature. However, to qualify SMS as a fertilizer, trace metals quantification must be performed to comply with the aforementioned regulations. It should once more be pointed out that the new amendment act (EU 2022/973) requires the evaluation of TI. In fact, although it is not used as an alloying agent in the steel industry, it can enter the steel production cycle through the raw materials (iron ore, coals, and fluxes) and comes out mainly as a

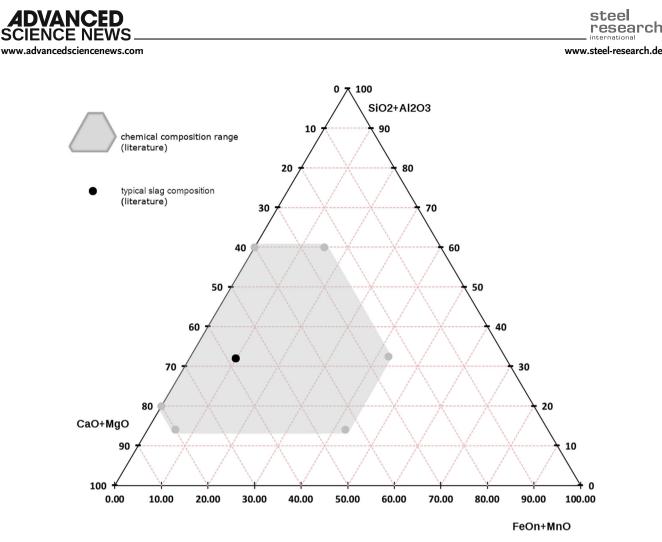


Figure 1. Composition diagram for secondary metallurgy slag. The colored area is based on compositional data from all European marketed ferrous slag covered by the RFSC-Consortium.

 Table 5. Typical chemical composition range of secondary metallurgy slag (wt%).

	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	FeO <sub>x</sub>	MnO	S	Cr <sub>2</sub> O <sub>3</sub>	Other (F, TiO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub> )	CaO <sub>free</sub>	MgO <sub>free</sub>
Min-max	35–60	5–30	4–37	4–13	0.5–10	0.1–10	0.1–4	0.03–5	≈5	≈10	≈6

powder in quantities on the order of hundreds of mg/t of crude steel produced.  $^{\left[ 54\right] }$ 

Some of these slag can self-disintegrate into a fine powder while others can completely crystallize or vitrify.<sup>[14]</sup> This depends upon the cooling rate and the mineralogy of the slag that is determined by the deoxidation procedure used to clean the steel, that is, Si- or Al-killed steels (**Table 6**).

Generally, calcium silicates can be present in a fraction greater than the 40 wt% whereas calcium aluminates are in the range 10–15 wt%. However, for some specific chemical composition, the aluminates can occupy up to the 60 wt% of the slag.<sup>[14]</sup>

As the mineralogical composition of such slag is mainly formed by silicates and aluminates, this slag can potentially dissolve in water and thus carry some nutrients to the plants or correct soil acidity. In addition, the presence of free CaO and free MgO lets them to generate strong alkaline pH (11.5–12.5).<sup>[13,55]</sup> Calcite, portlandite, brucite, and other hydroxides are typical phases of seasoned slag, that is slag exposed to environment for long time or accelerated by cooling them with water sprinklers. These mineral compounds are formed firstly by the reaction of free CaO and MgO with water and then with  $CO_2$  based on the Reaction (1), (2), and (3)<sup>[56]</sup>

$$CaO + H_2O \rightarrow Ca(OH)_2$$
 (1)

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
 (2)

$$MgO + H_2O \rightarrow Mg(OH)_2$$
 (3)

To confirm the low environmental risk potential, leaching test results of several secondary metallurgy slags found in the literature are given in **Table 7**. As predicted, SMS leaches very low concentrations of metals with respect BOFS or EAFS,<sup>[41,57]</sup> thus confirming that the reducing thermodynamic conditions taking place during the steel refining hardly bring leachable elements into the slag.

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Table 6. List of typical minerals featuring secondary metallurgy slag. Common minerals can be found in both siliceous and aluminous slag.<sup>[12,14,63–65]</sup>

Common	minerals	Silice	ous slag	Aluminous slag		
Periclase	MgO	Bredigite	$\alpha$ -Ca <sub>2</sub> SiO <sub>4</sub>	Spinel	$MgAl_2O_4$	
Lime	CaO	Larnite	$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub>	Mayenite	Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub>	
Anhydrite	CaSO <sub>4</sub>	Belite	$\gamma$ -Ca <sub>2</sub> SiO <sub>4</sub>	Celite	$Ca_3Al_2O_6$	
Wustite	(Fe.Mn.Mg)O	Alite	Ca <sub>3</sub> SiO <sub>5</sub>	Gehlenite/Melilite	Ca <sub>2</sub> Al(AlSi)O <sub>7</sub>	
Calcium ferrite	$Ca_2Fe_2O_5$	Diopside	MgCaSi <sub>2</sub> O <sub>6</sub>	Larnite	$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub>	
Fluorine	CaF <sub>2</sub>	Merwinite	$Ca_3Mg(SiO_4)_2$	Belite	$\gamma$ -Ca <sub>2</sub> SiO <sub>4</sub>	
Portlandite	Ca(OH) <sub>2</sub>	Akermanite	Ca <sub>2</sub> Mg(Si <sub>2</sub> O <sub>7</sub> )	-	-	
Calcite	CaCO <sub>3</sub>	_	-	-	-	
Brucite	Mg(OH) <sub>2</sub>	_	-	-	-	
Glass phase	_	-	_	-	-	

Table 7. Leaching behavior of different secondary steelmaking slag compared to the Italian regulation (values expressed in mg kg<sup>-1</sup>).

Standard	Reference	As	Ва	Be	Cd	Co	Cr	Cu	Hg	Мо	Ni	Pb
DIN 38414 S4	Gomes et al. <sup>[13]</sup>	<0.5	-	-	<0.04	-	0.6	0.52	<0.01	-	0.32	<0.5
DIN 38414 S4	Sofilić et al. <sup>[66]</sup>	<0.001	5.92	-	0.002	-	0.15	0.07	<0.001	<0.01	0.04	<0.01
EN 12 457-4	Loncnar et al. <sup>[58]</sup>	-	<0.26	-	-	-	<0.8	-	-	<1.4	-	-
EN 12 457-4	Xu et al. <sup>[67]</sup>	-	-	-	-	-	n.d.	n.d.	_	-	-	36.24
EN 12 457-2/3	Tossavainen <sup>[68]</sup>	-	-	-	-	_	0.08	-	-	0.008	-	
Limit values	D.M. 05/02/98 <sup>[50]</sup>	0.5	10	0.1	0.05	2.5	0.5	0.5	0.01	-	0.1	0.5
Standard	Reference	Sb	Se	V	Zn	$CI^-$	$CN^-$	$F^{-}$	I	NO <sub>3</sub> <sup>-</sup>	SO4 <sup>2-</sup>	тос
DIN 38414 S4	Gomes et al. <sup>[13]</sup>	-	-	_	0.98	_	_	-		-	-	-
DIN 38414 S4	Sofilić et al. <sup>[66]</sup>	<0.01	-	-	0.03	63	-	<1		-	10	36
EN 12 457-4	Loncnar et al. <sup>[58]</sup>	-	-	-	-	-	-	3.1–170		-	-	-
EN 12 457-4	Xu et al. <sup>[67]</sup>	-	-	-	21.22	-	-	-		-	-	-
EN 12 457-2/3	Tossavainen <sup>[68]</sup>	-	-	0.2	-	-	-	-		-	-	-
Limit values	D.M. 05/02/98 <sup>[50]</sup>	-	0.1	2.5	30	1000	0.5	15		50	2500	300

Although the strong alkaline environment developed by SMS dissolution should enhance the leaching of some cations (Ni, Cu, Cd, Pb, Zn) and anions (Mo, Cr, As, Se, Sb),<sup>[58]</sup> the concentrations of such toxic metals in the leachate remain low, definitively demonstrating the negligible environmental risk of such by-products.

# 4. Compliance of Secondary Metallurgy over Regulatory Framework

Since most of the secondary steel slag examined during the literature review meet the threshold values of the leaching tests (Table 7) and there are specific purposes for which they can be used, thus defining a reference market, they can cease to be considered as waste, in agreement with D.Lgs. 152/2006. In other words, SMS can be admitted to the simplified recovery procedures. Some limitations can rely with the high concentration of fluorides in the leachate for such slag where  $CaF_2$  is still used as flux. However, the use of fluorine is a practice that is

losing importance, in favor of the use of calcium-aluminatebased fluxes.<sup>[59]</sup> Registration to REACH with a positive outcome, entitles the manufacturing or import or use of this substance for specific products.

Secondary steelmaking slag chemical composition usually falls in the range requested for sameness check, as well as the mineralogical composition agrees with the requirements. For instance, the typical mineral compounds listed in Table 6 are in large amounts the same as requested for the sameness check for REACH registration. Thus, apart from special exceptions, the secondary steelmaking slag registration should be successful without particular difficulties.

With reference to "calcium-magnesium-sulfur-based fertilizers", the steelmaking slag possess all the requirements to be qualified as a calcium complex. As can be seen from the chemical composition (Table 5) and from the mineralogical composition (Table 6), the CaO concentration in such slag is abundantly higher than the requirements ( $\geq$ 15 wt% water-soluble CaO of which 8/10 in the form of a complex), as the CaO range from ADVANCED SCIENCE NEWS \_\_ www.advancedsciencenews.com

 Table 8. Solubility product constants of the major calcium compounds within steelmaking slag.

Mineral	k <sub>sp</sub>	Log [k <sub>sp</sub> ]	Reference
CaO	9.17·10 <sup>-6</sup>		Nicoleau et al. <sup>[69]</sup>
CaCO <sub>3</sub>	4.5·10 <sup>-9</sup>	-8.35	Chiang and Pan <sup>[70]</sup>
Ca(OH) <sub>2</sub>	5.5·10 <sup>-6</sup>	-5.19	Chiang and Pan <sup>[70]</sup>
MgCO <sub>3</sub>	3.5·10 <sup>-8</sup>	-7.46	Chiang and Pan <sup>[70]</sup>
Mg(OH) <sub>2</sub>	$1.8 \cdot 10^{-11}$	-11.1	Chiang and Pan <sup>[70]</sup>
Ca <sub>2</sub> SiO <sub>4</sub>	4.3·10 <sup>-18</sup>	-	Nicoleau et al. <sup>[69]</sup>
Ca <sub>3</sub> SiO <sub>5</sub>	9.6·10 <sup>-23</sup>	-	Nicoleau et al. <sup>[69]</sup>
$Ca_3Al_2O_6$	_	-74	Khaitan and Dzombak <sup>[71]</sup>
Ca <sub>3</sub> Al <sub>2</sub> H <sub>12</sub> O <sub>12</sub>	_	-22.3	Taylor <sup>[72]</sup>
C-S-H	$1.55 \cdot 10^{-14} - 5.71 \cdot 10^{-24}$	-	Glasser et al. <sup>[73]</sup>
CaS	8·10 <sup>-6</sup>	-	Table of Solubility
CaSO <sub>4</sub>	2.4·10 <sup>-5</sup>	-	Product Constants <sup>[74]</sup>
CaSO <sub>4</sub> ·2H <sub>2</sub> O	3.14·10 <sup>-5</sup>	-4.62	Chiang and Pan <sup>[70]</sup> and Table of Solubility Product Constants <sup>[74]</sup>

35 to 60 wt% and it is bound in reactive and water-soluble complexes such as calcium aluminates, calcium sulfide and dicalcium silicate (**Table 8**). As well, CaO is often present in the form of free lime (in some exception it can reach the 10 wt%). For these fertilizers, the declaration and addition of microelements is also allowed. Their declaration must respect the threshold values reported in Table 2. This aspect, however, had to be verified for each slag. Given the compliance of the steelmaking slag with the requirements for calcium-magnesium-sulfur-based fertilizers, there are no technical limitations for the inclusion of a new industrial fertilizer in the list of products permitted by the D.Lgs. 75/2010.

Secondary steelmaking slag also respect the requirements for their use as additive to national (Italian) fertilizers for increasing the concentration of secondary- (CaO, MgO, Na<sub>2</sub>O, and S) and micro-elements (Table 2). Since these elements feature the SMS, the use of this slag for this purpose could be considered. In particular, secondary steelmaking slag has CaO and MgO concentrations higher than the minimum declarable levels (CaO  $\geq 8$  wt% and MgO  $\geq 2$  wt%), while among the other meso-elements that can be declared, Na and S should be evaluated time by time.

Secondary steelmaking slag also complies with the requirement for their application as corrective, especially about the limits on toxic metals concentration (Table 3), regarding both the national (Italian) and the European frameworks. In addition, SMS can be produced with precise granulometry, thus fulfilling one of the classes of corrective provided by the D.Lgs. 75/2010.

Furthermore, referring to the chemical composition of SMS (Table 5), the high concentration of CaO and the strong alkalinity could configure them as a suitable sanitizer for sewage sludge treatment if the pH value of the leachate is close to or higher than that of common calcium compounds used for such a process and the amount of toxic metals leached is within the thresholds imposed by regulations, with most of the SMS characterized in literature already complying with the latter parameter

(Table 7). On the contrary, as with secondary elements, the particle size distribution as well as the pH and conductivity of the leachate are not usually reported in the literature regarding the characterization of SMS. Accordingly, the following section reports the complete characterization of 16 SMS samples specifically carried out to support the possible use as fertilizers.

# 5. Case Study

#### 5.1. Materials and Methods

Sixteen industrial derived SMS samples were used for the analysis required to determine their feasibility as fertilizers. They were sampled every two months to check for any heterogeneity or variation over time.

The general chemical composition was measured by wavelength dispersive X-ray fluorescence (WD-XRF) on 10 grams of sample dried at 105 °C for 24 h using a Bruker Tiger S8 spectrometer. Secondary elements, trace elements, and toxic metals were determined in accordance with the Italian fertilizer regulations by dissolving the sample in hydrochloric acid (HCl) and measuring the different elements as shown in **Table 9**.

Residual moisture at 105 °C and dry residue at 600 °C were determined in accordance with EN 14 346:2006 and EN 15 169:2007 standards, on the basis of Equation (4), (5), and (6)

$$m_{\rm DR} = \frac{m_{\rm c} - m_{\rm a}}{m_{\rm b} - m_{\rm a}} \times 100$$
 (4)

$$m_{\rm w} = 100 - m_{\rm DR} \tag{5}$$

where  $m_{\text{DR}}$  is the dry residue of the sample,  $m_{\text{c}}$  is the mass of the crucible containing the dried sample,  $m_{\text{b}}$  is the mass of the crucible containing the sample as it is (undried),  $m_{\text{a}}$  is the mass of the empty crucible, and  $m_{\text{w}}$  is the water content (residual moisture) of the sample

$$m_{\rm LOI} = \left[\frac{m_{\rm b} - m_{\rm c'}}{m_{\rm b} - m_{\rm a}} \times 100 - (100 - m_{\rm DR})\right] \times \frac{100}{m_{\rm DR}} \tag{6}$$

where  $m_{\text{LOI}}$  is the loss of ignition of the sample (dry residue at 600 °C) and  $m_{c'}$  is the mass of the crucible containing the ignited sample.

Crystallographic characterization was conducted on approximately 2 grams of sample dried at 105 °C by X-ray diffraction with a Bruker D2 Phaser Recognition of the identified crystalline phases was performed by Crystal Impact Match software using the crystallographic open database (COD).

The sample granulometry was evaluated by means of gradation curve using 8 sieves of increasing opening (0.045, 0.063, 0.09, 0.2, 0.5, 1, 2, 4, 8, and 10 mm).

Leaching test, determination of the pH value and the electrical conductivity (EC) were carried out in accordance with EN 12 457-2:2002 standard, adopting a liquid/solid ratio equal to10 L kg<sup>-1</sup> and keeping the distilled water/SMS sample solution stirred at 10 rpm for 24 h. Before measurement, the solution was allowed to decant for 1 h. Leached elements concentration was determined through ICP-OES/MS analysis, while pH and EC was carried out with an XS PC 52 + DHS pH meter-conductor calibrated on three points with ASTM standard solutions. A control analysis was carried out in the same manner with calcium carbonate.

# 

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	В	S	Co	Fe	Мо	Mn	Na	К	Р	С	N
ICP-OES	х	-	х	Х	-	х	-	х	-	-	-	х	-	Х	х	х	х	-	-
ICP-MS	-	х	х	Х	Х	х	х	Х	х	-	Х	-	Х	-	-	-	-	-	-
AAS	-	-	-	-	-	-	-	-	-	-	-	х	-	Х	Х	-	х	-	-
EA	-	_	-	-	-	-	-	-	-	Х	-	-	-	-	-	-	-	х	х

ICP-OES/MS: Induced Coupled Plasma – Optical Emission Spectroscopy/Mass Spectroscopy; AAS: Atomic Absorption Spectroscopy; EA: Elemental Analysis by ELTRA CS (for C and S) and ELTRA OHN (for N in inert atmosphere).

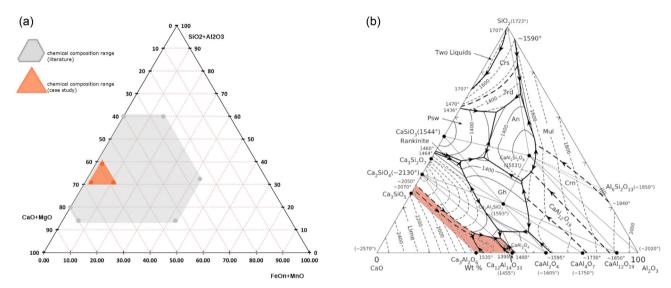


Figure 2. a) Displaying of the experimental chemical composition of the investigated secondary metallurgy slag (orange area) and comparison with the compositional data from all European marketed ferrous slag covered by the RFSC-Consortium (grey colored area) and b) expected mineralogical composition.

### 5.2. Result

### 5.2.1. General Chemical Composition and Mineralogy

**Figure 2**a (chemical composition) and Figure 2b (expected mineralogy) demonstrate the compliance of the 16 SMS samples under examination to the REACH and CLP regulations, thus the EINECS (266-004-1) and CAS (65 996-71-26) numbers specific for this kind of product can be assigned. This means that this slag can be commercialized as chemicals at communitarian level.

Indeed, based on the higher concentration of alkaline compounds (CaO plus MgO: 60–70 wt%) respect to the acidic ones (SiO<sub>2</sub> plus Al<sub>2</sub>O<sub>3</sub>: 30–40 wt%) and the other main oxide compounds (FeO<sub>x</sub> plus MnO: 30%–40%) the expected mineralogy of the 16 SMS samples is composed of mostly calcium-aluminate compounds. Specifically, the XRD patterns of the samples confirmed (**Figure 3**) the presence of mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) as the main component followed by hydrated compounds like hillebrandite, hydrogarnet, portlandite/brucite, and gypsum. They are respectively originated from the reaction of calcium silicates and aluminates, free lime/magnesia, and calcium sulfides originally present in the SMS samples with ambient moisture. The semi-quantitative assessment of the average amount of each compound within the SMS samples, based on the comparison between the XRD pattern and WD-XRF analysis, is given in **Table 10**.

The results of the analysis confirmed the preliminary conclusions highlighted by the literature review conducted earlier, thus reinforcing the little or no problems that SMS manufacturers would encounter in the REACH registration process.

Furthermore, since the concentration of hazardous elements in the leachate is far below the limits defined by D.M. 05/02/98 (Figure 4), the SMS samples examined are fully compliant with the simplified recovery procedures for bulk granulated slag; consequently, their marketing in Italy is permitted.

# 5.2.2. Agricultural Use Feasibility

To investigate the actual feasibility of introducing SMS in the agricultural field, the chemical and physical properties of the 16 SMS samples were compared with the thresholds established by the national and regional regulations for their suitability as chemical stabilizers and sanitizers for sewage sludge, fertilizers, and soil correctives (e.g., liming materials) or soil improvers.

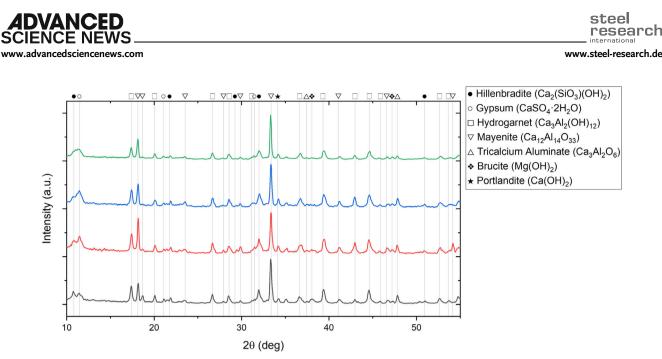


Figure 3. Diffraction patterns of the four secondary metallurgical slag considered most representative.

**Table 10.** Average semi-quantitative breakdown of compounds within the secondary metallurgical slag samples, estimated from the composition measured by WD-XRF and XRD patterns.

	Calcium aluminates	Calcium silicates	Gypsum	Calcium hydroxide	Magnesium hydroxide
Wt%	70	10	4	<1	8

#### 5.2.3. Chemical Stabilizers and Sanitizers for Sewage Sludge

One of the treatment operations required by both D.M. 29/01/07and by Appendix 4 of the Lombardy Region Resolution of 01/07/2014 (D.G.R. X/2031) consists of the chemical treatment with lime of the sludge necessary to bring the pH of the treated mass to 12 for a certain period of time. Consequently in **Table 11** is given the comparison of the leachate pH and conductivity of the 16 SMS samples after 24 h contact between water and slag at  $10 L kg^{-1}$ , in comparison with those of limestone and lime.

The pH value of the SMS samples leachate is largely over 12. As a consequence, the replacement of lime with a lime-based product, such as a secondary steelmaking slag, appears more than possible. In fact, SMS and fresh lime seem behave in the same way regarding pH, with only small differences in favor to lime. This means that the high amount of CaO featuring the SMS controls the pH like fresh lime. Still from the leachate properties comparison, a significant difference between lime and SMS against limestone is highlighted. This implies that

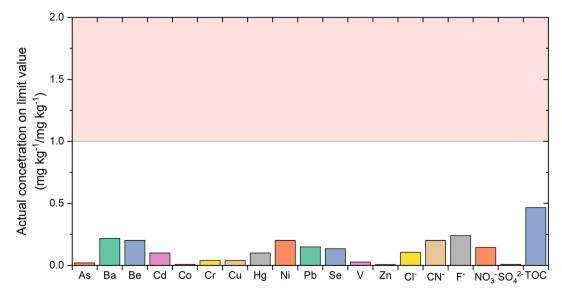


Figure 4. Average leached concentration of elements and compounds requested by Italian legislation (values expressed as the ratio between the maximum concentration measured in the leachate and the D.M. 05/02/98 limits).

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SMS samples, limestone, and lime.

	Leachate pH (standard deviation)	Conductivity [mS cm <sup>-1</sup> ] (standard deviation)
SMS (present work)	12.35 (0.09)	7.78 (0.47)
Coarse lime	12.46 (0.02)	8.61 (0.29)
Micronized lime	12.45 (0.02)	8.65 (0.31)
Limestone	9.98 (0.05)	0.059 (0.02)

Table 11. Comparison of the leachate pH and conductivity among the 16

SMS can behave better than limestone as a sanitizing agent for sewage sludge.

In Figure 5a is given the ratio between the maximum amount of the toxic metals observed in the 16 SMS samples and the limit values of the Italian legislation (Lombardy Region Resolution of 01/07/2014, D.G.R. X/2031); whereas Figure 5b shows the values of the fertilizing elements with respect to the requirements that treated sludge must meet for suitable use in agriculture, expressed as the ratio between the minimum value observed in the samples and the minimum legal limits.

The maximum concentrations of toxic metals observed in the 16 SMS samples fully comply with the limits imposed by D.G.R. X/2031 regarding their application as stabilizers for compliant sludge. In contrast, some limitations may arise for application as a stabilizer of high-quality sludge, as both As and Ni reached a value above their respective legislative limit. Luckily, the limits have to be evaluated also to the stabilized final product (sludge plus lime-based stabilizer). In other words, since the addition of the stabilizer is proportionate according to the needs of the sludge, the measured concentrations of each toxic elements will necessarily undergo dilution, thus going in favor of the SMS suitability as also high-quality sludge stabilizer.

Finally, although the concentration of C, N, and P does not exceed the minimum levels required by D.G.R. X/2031 and D.Lgs. 75/2010 for a suitable use in agriculture, it should be noted that also in this case this is referred to the final stabilized product. Consequently, these concentrations can still contribute to increasing the fertilizing power of a high-C, -N, and -P sludge, positively improving the supply of nutrients to the soil.

#### 5.2.4. Fertilizer

While the chemical composition of the 16 SMS samples confirms (Figure 2a) their qualification as calcium complexes and classification as "calcium-magnesium-sulfur fertilizers" according to the Italian legislation, as also previously pointed out in the literature review discussion, their declaration must comply with the minimum values given in D.Lgs. 75/2010, especially with regard to micro-element concentration. Figure 6 shows the values of micro-elements expressed as the ratio between the minimum observed values and the minimum legal limits for SMS application as fertilizers.

The results pointed out that the SMS samples possess four (Cu, Zn, Fe, and Mn) of the seven declarable trace elements for vegetable or nebulization fertilizer application, while it does not meet the B, Co, and Mo thresholds (Figure 6a). Conversely, if the comparison is extended to the minimum limits of the whole field or pastures, only the Fe threshold would be met (Figure 6b).

Nevertheless, it is worth mentioning that still in D.Lgs. 75/ 2010 (Annex 1 Chapter 2.6), the addition of both meso-elements (CaO, MgO, Na<sub>2</sub>O, and S) and trace elements (Cu, Zn, Fe, Mn, B, Co, and Mo) to already codified fertilizers is allowed. Therefore, as far as the fertilizer context is concerned, the application of the analyzed SMS would be feasible as an additional source of mesoelements to the currently codified Italian fertilizers (D.Lgs. 75/ 2010, Chapter 8) rather than as a fertilizer themselves. Similar considerations apply to the four trace elements that meet the threshold values.

Figure 7 shows the ratio between the maximum concentration of toxic metals observed in the 16 SMS samples and the limit values established by the European legislation for a possible marketing of SMS as inorganic fertilizers outside Italy.

The results showed that the 16 SMS samples complied with EU Regulation 2019/1009, with all toxic elements below the imposed thresholds. It should be noted that the new delegated act (EU 2022/973) was not in force at the time of the analysis (year 2020), hence Tl and V concentrations were not measured. On the contrary, the concentration of Tl and V measured by Pietrini et al.<sup>[60]</sup> within a LF slag came to a maximum amount of 0.1 and 106 mg kg<sup>-1</sup>, respectively, thus widely meeting the

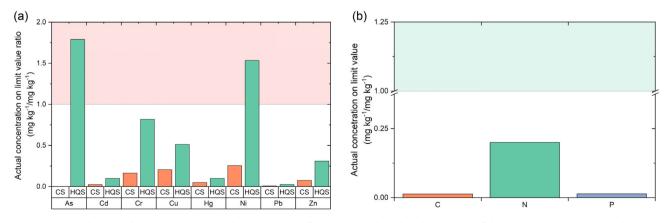
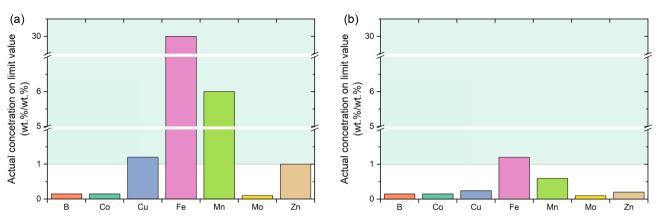


Figure 5. a) Ratio between the maximum measured concentration of the toxic metals and the limit values of the Italian D.G.R. X/2031 legislation (CS: compliant sludge, HQS: high-quality sludge); b) ratio between the minimum measured concentration of the fertilizing elements and the minimum thresholds required by the Italian D.G.R. X/2031 legislation.





**Figure 6.** Ratio between the minimum of measured micro-elements concentration and the minimum legal limits for SMS application as fertilizers (D.Lgs. 75/2010): a) for vegetable or nebulization application; b) for whole field or pastures.

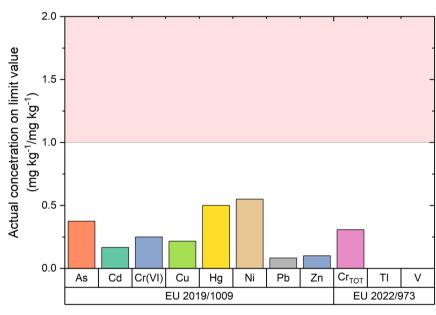


Figure 7. Ratio between the maximum measured concentration of metals and toxic compounds and the limit values of European legislation for inorganic fertilizers.

limits imposed by the delegated act. This encourages to push forward the evaluation process of approving the use of SMS as a fertilizer at both the Italian and European levels.

### 5.2.5. Soil Corrective (Liming Material) or Soil Improver

Given the overall chemical composition of the SMS samples analyzed (Figure 2a), they already possess the main qualities to be used as soil correctives and improvers. Indeed, SMS samples shown a liming treatment capacity similar to those of lime and limestone, with a corrective capacity able to persist over time and not end in the first days of SMS use due to the slow and continuous solubility of the minerals in the slag that provides lasting remedial action, as also evidenced by Deus et al.<sup>[61]</sup> Specifically, their results showed an improvement in the chemical properties of an acidic tropical soybean growing soil over a period of  $23 \ months$  and despite the introduction of heavy metals into the soil, the associated increase in pH hindered their availability.

The main limitations in the use of SMS as correctives are based on the maximum permissible concentrations of toxic elements specified in EU 2009/1009 and D.Lgs. 75/2010. Figure 8a shows the relationship between the maximum concentration of toxic elements measured in the 16 SMS samples and the legislative limit values (the most stringent thresholds were used for the comparison). Furthermore, since the concentrations of Cd, Cr(VI), and Hg were below the detection limit of the instrument (0.5 mg kg<sup>-1</sup>), their values were arbitrarily set at 0.49 mg kg<sup>-1</sup>. Finally, in Figure 8b is given the grading curve required for the classification of the corrective class (powder, shred, crude, and granular product) in case of compliance.

The SMS samples fully comply with the maximum admitted concentration of toxic elements specified by the Italian and the



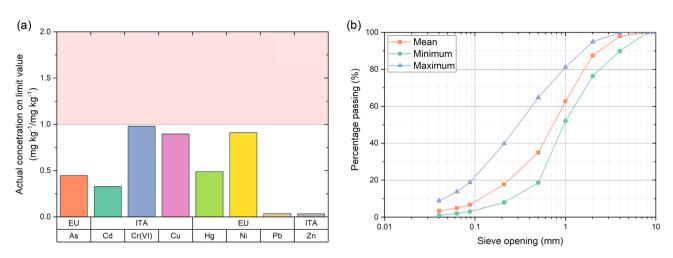


Figure 8. a) Ratio between the maximum measured concentration of toxic elements and the most stringent limit values of EU and/or Italian legislations (EU: EU 2009/1009, ITA: D.Lgs. 75/2010); b) experimental grading curve of the investigated SMS samples.

European regulations. Furthermore, according to the granulometry curve they could be qualified either as a shred, crude, or granular product.

It is worth noting that prior to the revision of Annex 3 of D.Lgs. 75/2010, occurred in September 2023, the Italian legislation did not allow the production of calcium-magnesium-based corrective agents and industrial products other than those from the production of lime with its own minerals. Specifically, thanks to the characterization performed on the 16 SMS samples and the deposition to the Italian Agriculture Ministry of a request of evaluation for a new corrective product, the Annex 3 was amended and now the possibility of also using a product derived from secondary metallurgy and in particular "white slag from electrical steel mill for the production of flat-rolled steel products with low phosphorus and sulfur content" came into force. Specifically, to be classified as such, the SMS must possess a minimum amount of CaO and MgO equal to 50 and 6.5 wt%, respectively (absolute percentage expressed as 0.7 for both of them) and at least the  $80^{\text{th}}$  percentile of grain size distribution less than 5 mm (crude product).<sup>[62]</sup>

Finally, the experimental tests required by the legislative process have shown that a SMS slag-based corrective can be easily distributed in "open field" with results comparable to those of commercial products in terms of both quantity and homogeneity (optimal and spatially uniform yield in the field). In fact, as with any corrective product or fertilizer, product distribution can be easily adjusted by opening and closing slots in the distribution system.

### 6. Conclusions

The literature review and the experimental characterization of a batch of 16 secondary steelmaking slag samples allow to conclude that: 1) secondary metallurgy steelmaking slag are suitable for the production of inorganic calcium-magnesium-sulfurbased fertilizers. Some micro-elements like Fe, Mn, Cu, and Zn may be also declared in the fertilizers composition; 2) secondary steelmaking slag may be used as additive to bring secondary elements (CaO, MgO) and micro-elements (Cu, Zn, Mn, Fe) to other types of national fertilizers; 3) secondary steelmaking slag can be used as a corrective for soils (calcium-magnesiumsulfur-based corrective) since they comply with the constraints on toxic metals (Cd, Cr(VI), Cu, Hg, Ni, Pb, Zn); 4) secondary metallurgy steelmaking slag have a corrective power equal to limestone and this effect lasts over time; 5) secondary metallurgy steelmaking slag are a suitable alternative to fresh lime for agricultural sewage sludge stabilization and sanitization, because they are a lime-based product with strong alkalinity and have a toxic metals concentration (As, Cd, Cr, Cr(VI), Cu, Hg, Ni, Pb, and Zn) below the threshold; 6) the case study demonstrated that the approach followed is correct and leads to formal approval of the use of an SMS slag-based corrective at the Italian level; and 7) the next step to be pursued at both the Italian and European level, is to obtain formal approval for the use of SMS to produce a new inorganic calciummagnesium-sulfur fertilizer.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# Data Availability Statement

Research data are not shared.

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### **Keywords**

fertilizer, sanitizing and pH correction, secondary metallurgy steelmaking slag, sewage sludge, soil corrective

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