

Laboratory investigation of Waelz slag stabilization

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1. Introduction

EAF dusts (EAFD) are one of the most important raw materials used to extract impure zinc oxide even though they are considered hazardous waste by both the European and American environmental protection agencies, as indicated in the European Waste Catalog (2002) and Catalog of Hazardous and Solid Waste (2004). The main reason for this classification is the high content of heavy metal (lead, cadmium and selenium) that can be easily released into the environment and cause serious health problems.

In the European Union, steel industries produce more than 1,000,000 tons/year of EAFD. This amount can be recycled by the Waelz process, which converts the dust into impure zinc oxide (Waelz oxide), which is then reprocessed in metallurgical plants, i.e. the imperial smelting process. The Waelz process is the most diffused in the world and is noted in the BREFs notes (Best Available Techniques Reference Document) of the European community as the Best Available Technology (BAT) for EAF dusts treatment (2013). After mixing EAFD with coke breeze (a reducing agent) and other additives (lime or siliceous sand), this charge is continuously

introduced in a rotary kiln. The high temperatures reached in the furnace allow the reduction and the vaporization of zinc and other volatile metals (lead and cadmium) to recover the Waelz oxide after oxidation-condensation processes. In Europe, the total amount of zinc, recovered through this technique, is about 250,000 tons/year. The molten residues, featured by low zinc and lead concentration, are water cooled at the end of the rotatory kiln to form granular Waelz slag. The recycling of all of the dusts produced in the EU could lead to the generation of nearly 800,000 tons/year of Waelz slag.

1.1. Waelz process

In a Waelz rotary kiln, three different zones can be identified (Fig. 1): in the first part, the temperature reaches approximately 600 °C allowing for the removal of charge humidity. In the second part, the temperature increases up to 1100 °C and chlorides start to volatilize and zinc-ferrites begin to decompose. Moreover, zinc, lead and iron oxide start to be reduced. In the last zone, the temperature reaches approximately 1300 °C and zinc and iron oxide are highly reduced. Zinc vapours are

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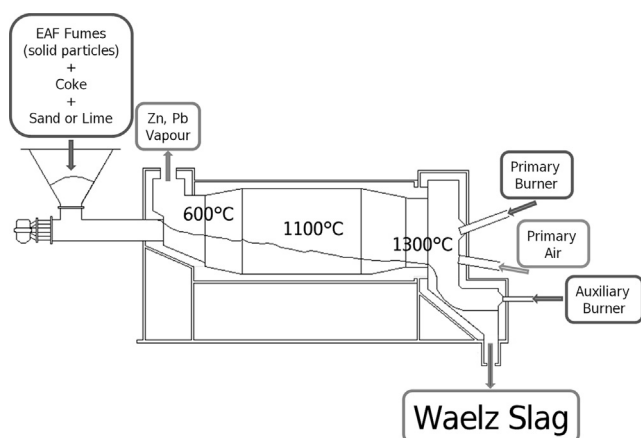


Fig. 1 – Waelz rotary kiln scheme.

aspired by an exhaust chimney and subsequently oxidized when they come in contact with air, producing the Waelz oxide.

Two different operative procedures can be followed during dusts treatment in the Waelz process: the addition of lime (basic running) or silica (acid running). In the first case, the kiln refractory duration is privileged whereas in the latter case, the Waelz slag reaches higher chemical stability and significantly reduces the lead releasing. Usually, the addition of silica is in the range of 14–18% by weight (Busè et al., 2014).

1.2. Waelz slag

Waelz slag is essentially an iron-reduced slag. Based on the mixture and composition of the material charged in the furnace, the operating conditions and the characteristics of the slag cooling, two different types of slag are obtained: silica-rich and lime-rich slags (Barna et al., 2000).

Even though the most of the zinc, lead and cadmium are removed and recovered during EAFD treatment, the Waelz slag is still classified as a dangerous and toxic waste due to excessive concentration of As, Cd, Cr⁶⁺, Cu, Pb, Ba and V (Barna et al., 2000). In particular, a typical Waelz slag produced after the basic running process is mainly formed by larnite (2CaO.SiO₂), calcium-ferrite, magnetite and wustite (Vegas et al., 2008; Quijorna et al., 2014). Specifically, calcium silicate, as reported by Barella et al. (2012) and Mombelli et al. (2013), is one of the phases major involved in heavy metal leaching, especially barium and vanadium.

Different studies have aimed to reduce the environmental impact of slag (in particular the EAF slag) through additional thermal, chemical or thermo-chemical treatments during or after the deslagging process. In particular, cooling rate effects on the leaching behaviour of steel slag were analyzed by Shinoda et al. (2008) and Tossavainen et al. (2007). They demonstrated that rapid cooling could improve slag stability, especially if coupled with correct chemical composition. MgO (Tossavainen et al., 2007) or combined (FeO + Al₂O₃ + MgO) (Drissen et al., 2009) additions were also studied in order to reduce chromium leaching, but with a detrimental effect on Ba, V and Se release. The addition of silica during deslagging operations, investigated by Barella et al. (2012) and Mombelli et al. (2012, 2013), seems to be the best technique to assure a safe and stable slag microstructure that avoids the release of the most dangerous elements. Since the polluting elements are generally bound to the silicates, reducing their amount or reducing their solubility are two ways to overcome the

problem. This could be achieved increasing the polymerization degree of the structure, namely increasing the number of SiO₄ tetrahedra. Specifically, the resistance of a silicate to hydration and the hydrolysis processes (in neutral conditions) increases with the degree of oxygen sharing between SiO₄ polyhedra of the mineral structure (Brantley et al., 2007).

A laboratory investigation was performed with the prospective of reducing the environmental impact of Waelz slag after disposal and expanding the possibility of its use in civil engineering applications as a replacement for conventional materials (Sorlini et al., 2004; Quijorna et al., 2011, 2012, 2014). For the Italian regulation, the recycle of hazardous waste coming from metallurgical industry requires the compliance of very strict limit on heavy metal leaching reported in “D.M. 03 August 2005 N. 201: definition of the criteria for waste acceptance at landfills” and “D.M. 05 April 2006 N. 186: identification of non-hazardous waste subject to simplified recovery procedures”. Italian laws specify the leaching test to be performed to assess the leaching behaviour for such a by-product: EN12457-2 standard leaching test in deionized water.

The investigation activities were focused on defining the additive amount that should be added to EAFD in the Waelz process to avoid the release of dangerous chemical species.

In particular, following the same approach proposed for EAF slag stabilization, different pure crystalline quartz (SiO₂) amounts were tested, in a range between 17.5 and 22.5% by weight, as well as different thermal treatment times and cooling rates.

2. Experimental procedure

2.1. EAF dusts characterization

The EAF dusts were taken from a steel mill and their chemical composition was measured by XRF and checked by SEM-EDS analysis. The dust used in the experiment was sieved to obtain a size distribution of about 0.5–3 mm.

Crystallographic analysis and phases identification were carried out using a Philips PW 3710 diffractometer on EAFD powder obtained by ring mill grinding. The X-ray analyses were performed using K α 1.5418 Å radiation produced by copper tubes excited by 40 kV and 30 A. Data was collected from 10° to 90° 2 θ with a step size of 0.02° 2 θ . Peaks identification was performed by exploiting Crystal Impact Match software through the use of the Crystallographic Open Database (COD).

The morphological and microstructural characterization was performed by a Zeiss EVO50 Scanning Electron Microscopy (SEM), equipped with an Oxford Inca EDS probe. The EAFD were compacted and mounted in epoxide resin, ground and polished. SEM analysis was carried out using a backscattered electrons probe (BSE) in order to identify and check the different phases pointed out by XRD. The general and local chemical compositions were measured with an EDS probe.

2.2. Melting temperature identification

The preliminary investigations were performed using a wettability furnace, in order to identify the melting temperature of EAFD and to evaluate the optimal silica addition.

The solid residuals contained in the fumes were pulverized by a ring mill and mixed with different amounts of SiO₂ (0, 10, 20 and 30% by weight). For each condition, 50 mg of

Table 1 – Sample identification and relative experimental conditions.

Slag ID	% SiO ₂	Cooling	Treatment time
A-17.5-0.5	17.5	Air	30 min
A-17.5-1	17.5	Air	1 h
A-17.5-2	17.5	Air	2 h
A-20-0.5	20	Air	30 min
A-20-1	20	Air	1 h
A-20-2	20	Air	2 h
A-22.5-0.5	22.5	Air	30 min
A-22.5-1	22.5	Air	1 h
A-22.5-2	22.5	Air	2 h
W-17.5-0.5	17.5	Water	30 min
W-20-0.5	20	Water	30 min
W-22.5-0.5	22.5	Water	30 min

mixture was analyzed and four tests were carried out at 10 °C/min, using a Hot Stage Microscope MISURA equipped with MISURA 3.32HSM software.

These experiments aid in identifying the best range of quartz to be added, in order to reduce the charge melting temperature and to improve the efficiency of the Waelz process.

2.3. Laboratory Waelz slag production

Based on the results of the wettability furnace trials, three different amounts of SiO₂ addition were selected: 17.5, 20 and 22.5% in weight. The quartz powders were mixed with 130 g of the solid fraction contained in the fumes and treated in a laboratory furnace, for different times, at 1300 °C. All the experiments were performed in a silica-based crucible.

At the end of the thermal maintaining, the treated mass was cooled either in air or water to identify the cooling rate effect has on the microstructure. The designed experiments are summarized in Table 1.

Each sample of laboratory slag was characterized morphologically and microstructurally by SEM and XRD, as well as the as-received EAF dust.

2.4. Leaching tests

In order to classify the produced slag as safe, leaching tests on 100 g of granulated slag were performed in accordance with the EN 12457-2 standard.

The slag was crushed in agate mortar, sifted through a 4 mm sieve, mixed with 1 l of deionized water (10 l/kg liquid/solid ratio) and stirred at 10 rpm (rounds per minute) for 24 h by a rotary mixer.

At the end of the test, the water solution was filtered by a 0.45 μm vacuum system and analyzed by ICP-OES in

order to detect the released chemical species. The elements investigated and the relative concentration limits are recorded in Table 2.

A new set of leaching tests was performed, on the samples that comply the limit imposed by Italian regulations, varying the pH of the initial solution. The same procedure described in EN 12457-2 standard was adopted. The pH was varied from 5 to 12.5 using HNO₃ or NaOH to adjust the pH:

- pH 5: 0.5 ml of standard 65% HNO₃ diluted 50 times solution was added to 1000 ml of deionized water;
- pH 10: 0.5 ml of NaOH 1N diluted 50 times solution was added to 1000 ml of deionized water;
- pH 12.5: 5 ml of NaOH 1N diluted 50 times solution was added to 1000 of deionized water.

At the end of the test, the solutions were acidified by HNO₃ (1:10) and then filtered by a 0.45 μm vacuum system and analyzed by ICP-MS in order to detect the released chemical species.

3. Results

3.1. EAFD characterization

Macroscopically, the powders dragged and filtered by the fumes appeared crumbly, dusty and dark brown. The general chemical composition (Table 3), performed by XRF analysis and checked by SEM-EDS, was typical of EAFD coming from low-alloy carbon steel production, as confirmed by various research studies (Shawabkeh, 2010; Bruckard et al., 2005; Sofili et al., 2004; Machado et al., 2006).

SEM and XRD analysis pointed out the typical microstructure of powders obtained from carbon steel production (Shawabkeh, 2010; Bruckard et al., 2005; Machado et al., 2006; Lenz and Martins, 2007). The fragments constituting the powders are essentially composed of wustite ((Fe,Mn,Mg)O – W in Fig. 2) and larnite (2CaO·SiO₂ – L in Fig. 2), in which the secondary phases are dispersed, i.e. iron-zinc sulphides (S), calcinated magnetite (M) and complex spinels formed by the reactions between franklinite and chromite (Sp). The chemical composition of the identified phase is shown in Table 4. The XRD analysis also detects metallic iron and lead oxide not identifiable by SEM and in accordance with XRF chemical composition. Ni and Pb sulphides (Shawabkeh, 2010) have also been detected. Unfortunately these compounds have the same diffraction angles of (Fe,Zn)S rendering their identification imprecise.

Table 2 – Elements investigated and limits imposed by Italian D.M. 03 August 2005 N. 201 “Criteria for waste acceptance at landfills” and D.M. 05 April 2006 “Recovery of non-hazardous waste”.

Element	Ba	Cu	Zn	Be	Co	Ni	V	As	Cd	Cr	Pb	Se	Hg	pH
Limit [μg/l]	1000	50	3000	10	250	10	250	50	5	50	50	10	1	5.5–12

Table 3 – EADF chemical composition by XRF analysis (weight %).

Weight %	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	S	Cl	K ₂ O	CaO	TiO ₂
	0.81	2.25	2.69	7.80	0.34	1.71	0.98	0.40	18.07	0.19
Weight %	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃	Co ₃ O ₄	NiO	CuO	ZnO	PbO	
	0.10	2.11	3.47	45.80	0.02	0.13	0.40	11.47	0.90	

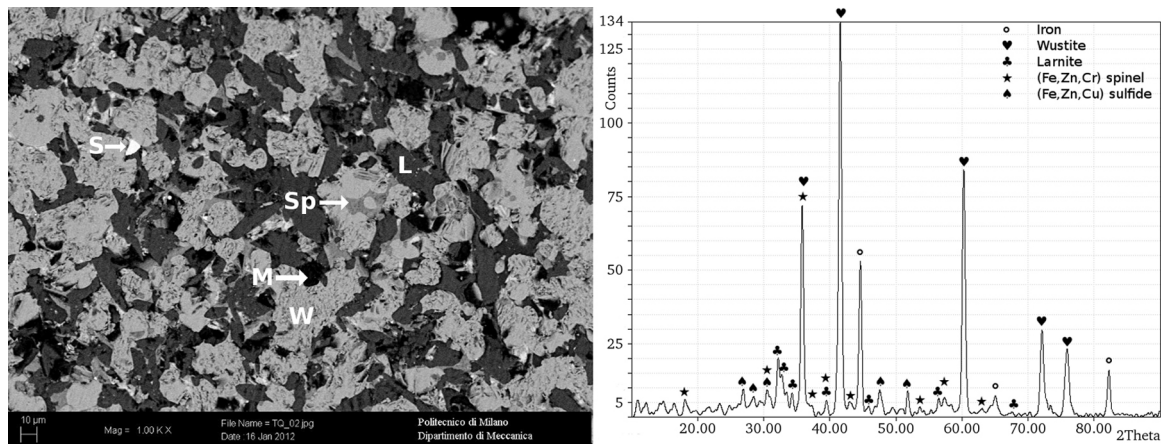


Fig. 2 – SEM-BSE picture and XRD pattern of as-received EAFD (L = larnite; M = calcinated magnetite; S = Zn,Fe sulphide; Sp = spinel; W = wustite).

3.2. Melting temperature identification

Despite the basic running is preferred because concerns high refractory life and increases the zinc yield, Waelz acidic running produces acid slag featured by a low lead concentration (Busè et al., 2014). However, the amount of silica added to the EAFD charge is not enough to hinder the release of other dangerous species, i.e. Ba and Cr (Barna et al., 2000). The best range of silica addition has been identified, thanks to the wettability furnace tests, and could lead to an increase in the efficiency of the Waelz process and stabilization of the produced slag.

Fig. 3 shows the various melting temperatures reached by the treated powders as a function of the silica addition. The graph shows a minimum between 17.5% and 22.5% of the added silica by weight. Thus, this range has been investigated through laboratory testing because a decrease in the melting temperature of the charged material (EAFD + SiO₂) can decrease the total amount of energy used during Waelz process, which can increase zinc recovery. Moreover the stabilization of the Waelz slag should be easily reached due to the high liquid phase present in the slag at the end of the process that lead high possibility to vitrify thanks to the water cooling.

The obtained values comply with those reported by Milella (2004) in his report. The liquid or semi-liquid treated materials improve the interaction among the silica and other phases. In particular, silica should react with larnite and iron oxide to form a complex ternary oxide insoluble in water. Moreover, if the iron oxide reacts with the silica, it should separate from the zinc oxide, which should easily reduce, increasing the amount of the recovered Waelz oxide (mainly constituted by ZnO).

3.3. Laboratory Waelz slag production

The aim of this work is to simulate the production of Waelz slag and the effects of silica addition during the process.

Laboratory simulation of the entire transformation occurring within a Waelz kiln is unfeasible for several reasons, i.e. scale factors. However, the results obtained can still be considered transferable to the real process. The reduction reactions, which occur at the top of the rotary kiln, should not influence the effect silica produces on the mass in the final section of the furnace.

3.3.1. Reference Waelz slag

Two reference laboratory Waelz slag were produced, exploiting the same procedure described in Section 2.3, in order to compare and evaluate the effect of silica addition on Waelz slag stability. The reference slag were defined as alkaline and acidic and were prepared adding 15% by weight of CaO and 15% by weight of SiO₂ to 100 g of EAF dusts, respectively. The chosen mixing ratio are comparable with those employed in basic or acidic running in actual Waelz processes.

Microstructurally, alkaline slag significantly differed to acidic slag (Fig. 4, Table 5). The alkaline artificial slag did not highly differ from a typical alkaline Waelz slag (Vegas et al., 2008; Quijorna et al., 2014). In fact, this sample is characterized by a calcium-silicate matrix (“CS” in Fig. 4a) where dendritic wustite (“W” in Fig. 4a) and Al-Fe-Cr-Zn spinel (“Sp” in Fig. 4a) are dispersed. On the contrary, acidic artificial slag exhibited a glassy matrix (“Gl” in Fig. 4b) where elongated Ca-Mg-Fe-silicates has grown (“Ol” in Fig. 4b). Complex Al-Fe-Cr-Zn spinel (“Sp” in Fig. 4b) was also detected. The acidic sample pointed out the presence of very small amount of wustite (“W” in Fig. 4b) and dispersed Fe-Zn-Pb-sulphides (bright dots labelled as “S” in Fig. 4b) in contrast to the correspondent alka-line slag. In particular, wustite seems to react with silica to form such as elongated silicates. Probably the addition of 15% by weight of quartz was not enough to complexate the total amount of iron oxide. This hypothesis is supported by the identification of Fe-rich areas along the lamellae (clear grey boundary in “Ol” lamellae in Fig. 4b). Moreover the melt-ing temperature of acidic slag is lower than the alkaline ones

Table 4 – SEM-EDS local chemical composition of as-received EAFD (weight %).

Phase	Mg	Al	Si	S	Ca	Cr	Mn	Fe	Zn	Pb
Fe,Zn Sulphide (S)				34.56	0.6		2.34	19.02	40.74	0.35
Wustite (W)	6.86				2.72	2.15	7.44	78.72	2.11	
Spinel (Sp)	4.29	10.48			13.21	17.87	3.88	45.26	4.4	0.16
Larnite (L)			23.56	0.61	67.48			1.05		0.22
Calcinated magnetite (M)	1.53		3.25	6.98	10.93	1.69	6.41	68.18	1.02	

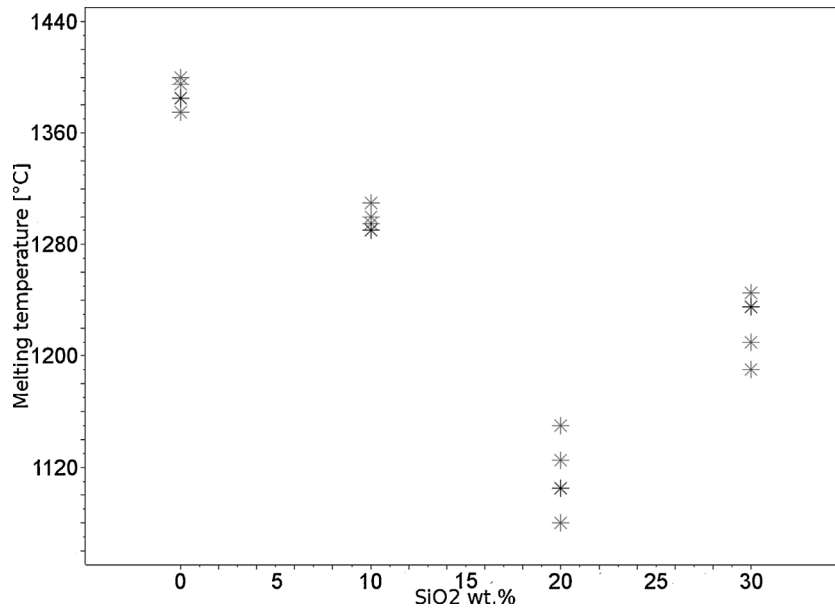


Fig. 3 – Melting temperatures of the modified and treated EAFD.

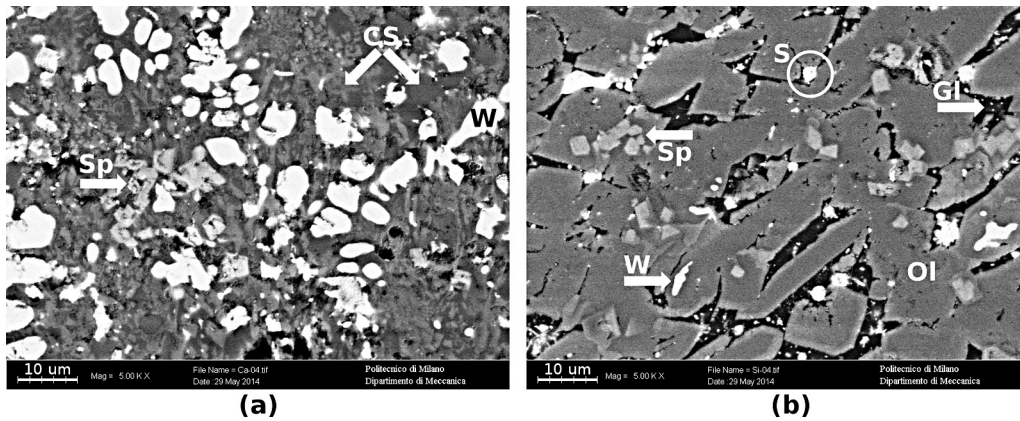


Fig. 4 – SEM-BSE pictures of reference Waelz slag: (a) 15% CaO; (b) 15% SiO₂. CS: calcium silicate; Gl = glass; Ol = olivine; S = sulphide; Sp = spinel; W = wustite.

(Milella, 2004), and this aspect seems to promote the nucleation and growth of sulphides into the glassy phase.

3.3.2. Modified Waelz slag

The artificial modified Waelz slag appeared black-grey, opaque and glassy, similar to common igneous rocks. Such slag has mechanical strength high enough to prevent its crushing by simple manual action.

From a microstructural point of view (Figs. 5 and 6), the effect of the silica was clearly evident: the phases morphology

was completely different when compared with the powder contained in the fumes and with the more common basic slag.

In the first series of artificial slag the time dependence was investigated (Fig. 5).

The samples, treated for less than 60 min, were featured by crystalline lamellar silicates (marked as “Ol” in Fig. 5a-b-d-e-g-h) dispersed in a glass matrix rich in silica (Fig. 5 – marked as “Gl”). As the maintaining time increased, these lamellar silicates changed their crystalline structure and their chemical composition, forming crystalline blocks inside the glassy

Table 5 – SEM-EDS local chemical composition of alkaline (15% CaO) and acidic (15% SiO₂) reference Waelz slag (weight %).

ID	Mg	Al	Si	S	Ca	V	Cr	Mn	Fe	Zn	Ba	Pb
Alkaline slag (15% CaO)												
Wustite (W)	3.09		0.81		1.00			4.40	85.97	4.11	0.62	
Spinel (Sp)	4.83	14.53			0.77	0.06	38.65	2.34	25.56	13.26		
Calcium silicate (CS)	2.72	5.19	25.28		40.88			2.70	18.57	4.41	0.25	
Calcium silicate (CS)	1.55	9.42	27.69		41.55			1.37	10.82	7.32	0.29	
Acidic slag (15% SiO ₂)												
Wustite (W)	1.42	1.11	5.95		4.29	0.42		2.19	78.07	5.84	0.70	
Spinel (Sp)	3.41	14.15	2.04		1.74	0.62	31.35	2.26	29.72	14.05	0.66	
Sulphide (S)		1.09	2.60	17.10	2.15				13.83	31.34		31.15
Olivine (Ol)	5.70		24.58		18.13	0.18		5.43	42.39	3.60		
Glass (Gl)		13.44	28.07	1.72	21.03				22.97	5.76		

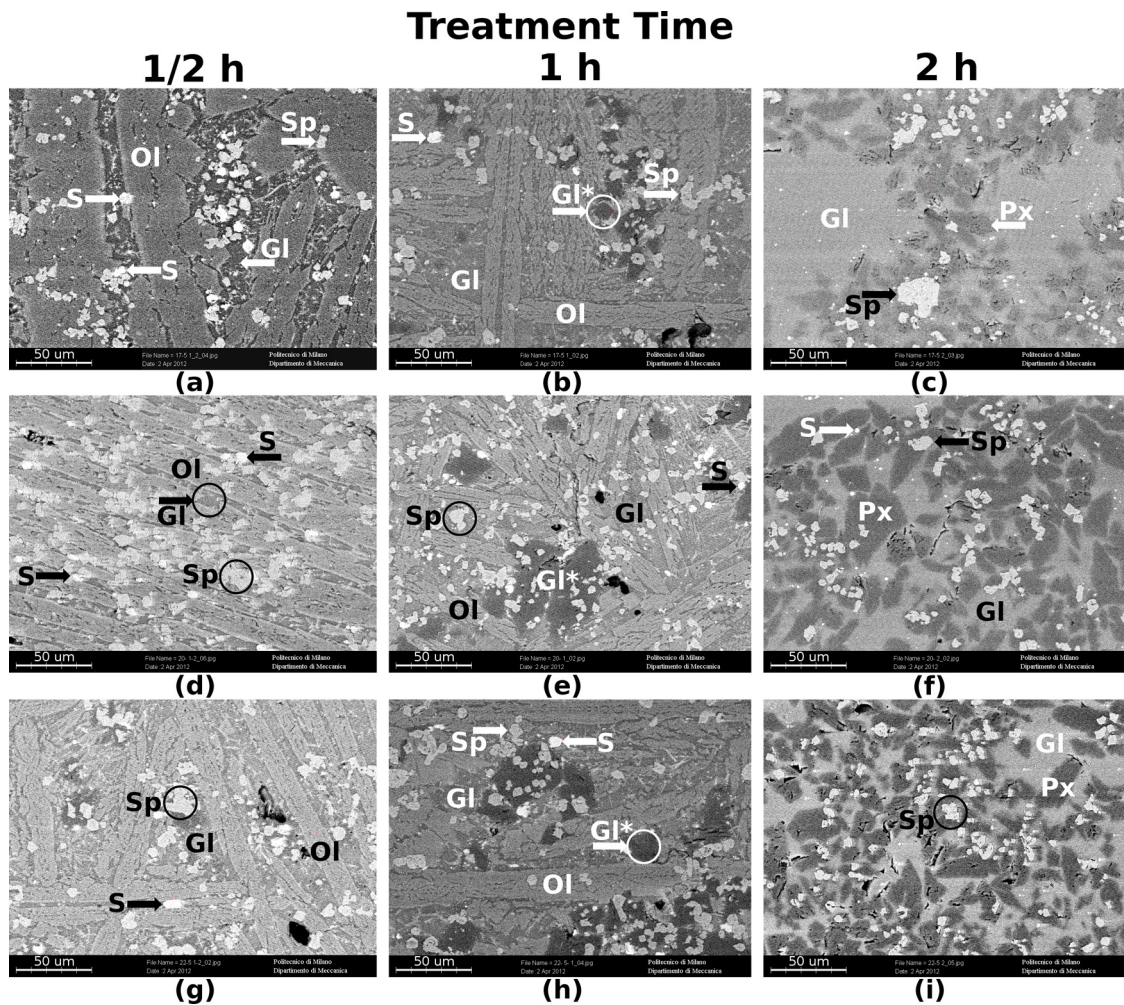


Fig. 5 – SEM-BSE pictures of air-cooled laboratory Waelz slag: 17.5% SiO₂ (a) 1/2 h, (b) 1 h, (c) 2 h treatment time; 20% SiO₂, (d) 1/2 h, (e) 1 h, (f) 2 h treatment time; 22.5% SiO₂, (g) 1/2 h, (h) 1 h and (i) 2 h treatment time. Gl = glass; Gl* = MgO enriched glass; Ol = olivine, Px = pyroxene; S = sulphide; Sp = spinel.

matrix (“Px” in Fig. 5c-f-i). The smaller and light grey phases (identified by “Sp” mark) dispersed within the various samples were complex oxides of aluminium, iron, chromium and zinc, featured by a spinel structure. The bright dots (marked by “S”) were iron, zinc, nickel, copper and lead sulphides featured by a different chemical composition, as reported in Table 6.

As the maintaining time was increased, the spinels size increased whereas the sulphides were dissolved in the glassy matrix. Moreover, only in the samples treated for 1 h, two different glassy phases could be pointed out: the first, marked as “Gl”, maintained the same composition of the initial glassy phase, whereas the second, indicated as “Gl*”, was enriched

in MgO (Table 6). Probably, this phase is a transition glass due to the transformation from elongated silicate (Ol) into the new crystalline blocks (Px).

XRD analysis and local chemical compositions allowed for identifying the nature of the crystalline phases revealed by SEM analysis. In the samples treated for times not exceeding 60 min, the elongated silicates belonged to the olivine family (Fig. 7a).

This diffraction pattern is typical of this kind of silicate in lamellae, as indicated by several authors (Poitrasson et al., 2009; Eliyahu-Behara et al., 2012; Piatak et al., 2004). The grown olivines are most likely a complex solid solution of Fayalite,

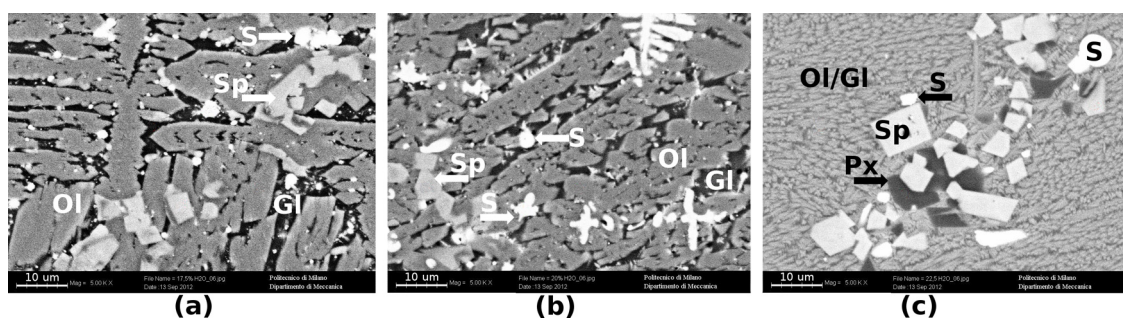


Fig. 6 – SEM-BSE pictures of water-cooled laboratory Waelz slag: (a) 17.5% SiO₂ 1/2; (b) 20% SiO₂ 1/2 h; (c) 22.5% SiO₂ 1/2 h treatment time. Gl = glass; Ol = olivine, Px = pyroxene; S = sulphide; Sp = spinel.

Table 6 – SEM-EDS local chemical composition of air-cooled laboratory Waelz slag (weight %).

	ID	Mg	Al	Si	S	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Ba	Pb	
17.5% SiO ₂				1.01	18.60	1.31				8.94		32.67			37.46	
		Sulphide														
		Sulphide				33.94					17.02	13.01				
	1/2h	Spinel	1.31	4.93				0.54	5.35	1.06	79.35			6.70		
		Olivine	6.57		24.82		13.80	0.20		5.22	42.76			6.63		
		Glass		3.67	29.88		21.65	0.02		1.51	35.01			7.13	0.42	
		Sulphide				29.80		0.10			6.39		11.03	46.21	0.29	6.19
		Spinel	1.65	5.56				0.51	2.43	1.33	79.92			7.78		
	1h	Olivine	6.70	1.09	24.55		8.87			5.25	45.59			7.48	0.47	
		Glass		4.98	28.92		18.36			2.71	30.33			10.11	0.15	
		Mg-glass	5.22	3.87	35.38		22.60		0.37	1.70	27.86			2.93	0.08	
		Spinel						1.50	66.15		19.53			12.58	0.24	
2h	Pyroxene	1.89	5.86	33.06		12.21			3.17	35.65			7.29			
	Glass	5.10		37.86		18.08	0.01	0.19	2.99	32.81			2.31	0.65		
20% SiO ₂					33.03					7.77			59.20			
		Sulphide						0.06	0.35			42.86	20.40	0.19		
	1/2h	Spinel	1.98	5.31				0.40	2.69	2.11	78.23		8.90	0.37		
		Olivine	4.24	2.06	26.48		17.75	0.31	0.25	3.82	37.27			7.82		
		Glass		8.02	31.30		22.76		0.14		22.92			9.55		
		Sulphide			2.12	26.85	1.74		0.02		13.15	4.13	2.62	41.26		8.11
		Spinel	2.09	5.98				0.44	37.08		39.02			15.08	0.30	
	1h	Olivine	6.57		25.27		8.80	0.09		5.85	48.21			5.20		
		Glass		3.64	32.84	1.41	19.51			1.58	25.84			13.94	0.40	
		Mg-glass	5.66	2.61	37.46		24.76	0.73	0.10	2.44	26.23					
		Sulphide			6.99	17.75	2.54	0.32	0.14		13.56	10.87	37.60	5.09		
	2h	Spinel		7.43				0.67	5.91	1.34	74.81			8.60	1.24	
	Pyroxene	4.42	6.08	34.97		18.98	0.36		3.18	28.11			3.88	0.02		
	Glass		6.11	29.58	2.26	9.96	0.36	0.16	2.82	32.10			15.09	0.17		
22.5% SiO ₂					26.38					8.32		61.26	3.29	0.78		
	1/2h	Spinel	2.27	15.35						41.49			15.56			
		Olivine	5.02	2.55	26.68		14.70			5.03	37.17			8.09		
		Glass	4.08	3.44	36.06		24.18			2.07	26.12			3.18		
		Sulphide				34.04		0.10			5.64			60.22		
		Spinel		5.24				0.78	15.92	2.13	66.18			9.46	0.28	
	1h	Olivine	3.97		25.97		10.26	0.10		5.49	46.38			7.84		
		Glass		5.36	29.55		19.11		0.08	2.95	29.57			9.83		
		Mg-glass	5.80	2.48	37.09		23.59			2.13	23.33			4.29	1.29	
		Spinel	1.93	6.12	1.76			0.54	34.60		39.32			15.72		
	2h	Pyroxene	5.17	5.43	35.96		18.41	0.04	0.31	2.83	28.75			3.11		
		Glass		5.84	29.97	3.04	8.40	0.26	0.49	2.62	29.64	3.00		13.49	0.05	

Forsterite and Calcium-olivines, due to the initial chemical composition (rich in CaO and FeO), the SiO₂ addition and the presence of other species, i.e. ZnO.

The diffraction patterns of samples treated for 2 h showed intense peaks associated with pyroxene phases (Fig. 7a). The experimental trials underlined that the reaction between silica and olivines at high temperatures starts only after 1 h.

XRD analysis also confirmed the dissolution of sulphides and the growth of Zn–Cr–Fe spinels.

The water cooled samples appeared similar to the air cooled slag. SEM analysis (Fig. 6, Table 7) showed the same structural constituents of the previous sample series but their dimensions were of a smaller order of magnitude.

It appears that the rapid cooling did not allow for the complete formation of olivines lamellae, which appeared dendritic. Moreover, as the silica concentration was increased, the lamellae extension decreased, whereas the zinc-iron-chromium spinel growth seemed to be favoured (Fig. 6a and b).

In the W-22.5-0.5 samples (Fig. 6c), the matrix was composed of alternated thin olivine lamellae and glassy phase in which large agglomerates of Fe–Zn–Cr spinel were detected. Polygonal crystals (marked by D) featuring the same

composition of pyroxenes found in air cooled slag were identified by SEM analysis.

The XRD patterns, related to these samples (Fig. 7b), had the same aspect as half-an-hour air-cooled slag (A-17.5-0.5), but the peaks appeared spread out and not well defined, likely due to the dendritic morphology.

Although SEM detected pyroxene-like phases in the W-22.5-0.5 sample, there was not enough fraction to produce intense diffraction peaks. On the contrary, the excess of silica lead to a significant formation of crystalline fraction greater than that found in the other cases. Intense peaks, associated with the spinel phase, confirm the agglomeration of these oxides. The short maintaining time and the fast cooling rate also prevented the sulphide dissolution.

3.4. Leaching tests

Only the values that overcome the regulation limits (Table 2) were reported, because of the other investigated elements listed in Table 2 (Be, Co, V, Ni, As, Cd, Se and Hg) were under ICP-OES detection limit.

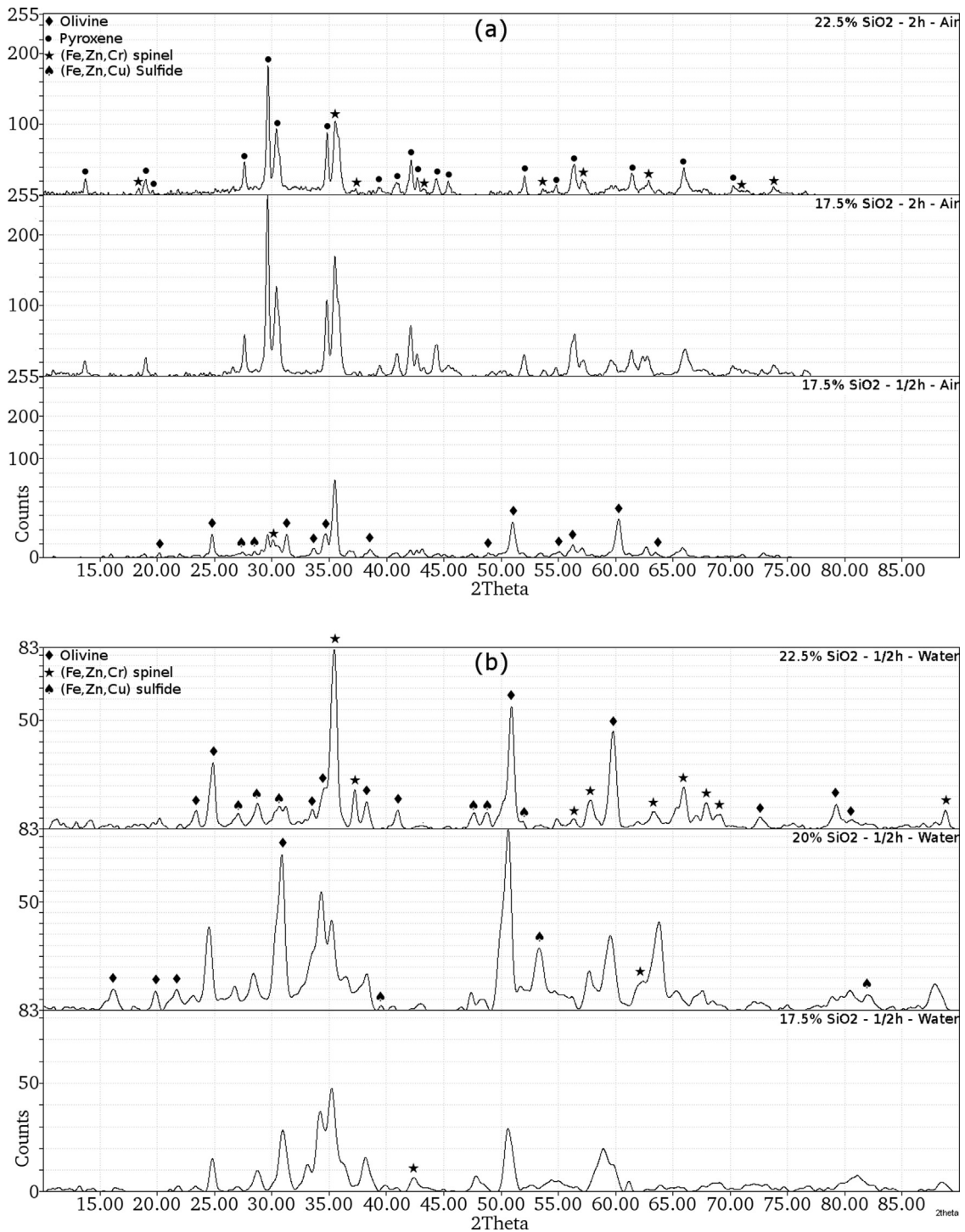


Fig. 7 – XRD pattern of (a) air-cooled and (b) water-cooled laboratory Waelz slag produced at 1300 °C.

3.4.1. Leaching test on EAFD

Water ICP-OES analyses, after the leaching test, show a high concentration of heavy metals in the elute solution (Table 8). Very high concentrations of chromium and lead, together with high levels of barium and zinc classify the EAF powder dragged by the fumes as a hazardous waste. Under these conditions, not only can EAFD not be recycled for other purposes (except for zinc and lead extraction in the Waelz process) but the Waelz slag is also affected by the same environmental problem, which excludes its re-use, as Barna et al. (2000) demonstrated very well.

3.4.2. Reference Waelz slag

Laboratory Waelz slag, considered as standard non-modified condition, showed lower release of the same elements than EAFD. Specifically, as expected, alkaline slag promote high release of Ba and Pb in the elute than the acidic slag (Table 8). On the contrary, acidic slag lead to higher concentration of leached zinc. These results complied with those reported in literature (Busè et al., 2014; Milella, 2004; Barna et al., 2000): although the basic process is preferred, due to the higher process yield and the less consumption of kiln refractory, it produces slag with high attitude to release lead. Moreover, due

Table 7 – SEM-EDS local chemical composition of water-cooled laboratory Waelz slag (weight %).

ID	Mg	Al	Si	S	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Ba	Pb
<i>17.5% SiO₂ – 1/2h – H₂O</i>														
Sulphide (S)		2.01	4.10	25.52	2.87	0.02	0.21	0.34	19.90			44.21	0.45	
Spinel (Sp)	3.13	12.05			0.60	0.93	37.20	2.05	30.83			12.83	0.08	
Olivine (Ol)	5.08	0.47	25.44		15.34	0.09	0.06	4.59	44.20			4.73		
Glass (Gl)	0.41	10.42	30.05	0.37	20.44	0.11	0.09	1.42	25.54			4.54	0.83	0.54
<i>20% SiO₂ – 1/2h – H₂O</i>														
Sulphide (S)		2.22	2.99		1.67	0.40	0.44	1.03	81.73			8.80		0.12
Sulphide (S)	0.58	1.71	11.71	17.50	8.80	0.11	0.68	1.40	23.26		0.03	33.74		
Spinel (Sp)	2.87	14.76			0.30	0.24	37.25	2.24	26.08			15.92		
Olivine (Ol)	5.23	0.40	24.89		16.18	0.02	0.16	4.74	40.62			5.76		0.56
Glass (Gl)		11.61	25.76	3.43	16.35	0.03	0.08	1.23	22.09			13.99	0.87	0.17
<i>22.5% SiO₂ – 1/2h – H₂O</i>														
Sulphide (S)					0.39		0.20		83.24	11.73	3.94		0.10	0.04
Sulphide (S)		0.33	0.75	32.50	0.42		0.12	0.18	29.35	3.55	27.67	4.19	0.12	0.81
Spinel (Sp)	2.33	18.23	2.39		1.89	1.29	27.09	1.29	23.29			18.30	0.01	0.61
Olivine in glassy matrix (Ol/Gl)	2.90	4.92	29.09	0.87	12.57	0.11	0.10	2.97	35.51			8.92	0.43	
Pyroxene (Px)	6.53	6.20	37.65		20.75	0.04	0.95	2.25	22.37			2.91		

to the high basicity of such a slag, the final solution pH reaches high values that enhance the lead dissolution (Houben et al., 2013; Pierrard et al., 2002).

3.4.3. Leaching test on air-cooled Waelz slag
A comparison of the elements released by the reference and the laboratory Waelz slag demonstrates the silica treatment efficiency (Table 8). Barium and zinc release in air-cooled artificial slag were lower than the limits imposed by Italian Law (Table 2) for all of the tested conditions. Otherwise, chromium, lead and copper release overcame the limits except for the sample added with the 20% by weight of silica. Fig. 8 summarizes the leaching test results for air-cooled slag. The A-20-0.5 sample clearly indicated the lowest concentration of the above-mentioned heavy metals for this slag group, and this trend reflects the final pH values reached by the water after the test.

3.4.4. Leaching test on water-cooled Waelz slag
Water-cooled samples reached higher stability than the air-cooled ones. Barium concentration in the leached solution was one order of magnitude lower than that revealed in the previous case and the other problematic elements, i.e. Cr, Pb and Cu, were under the ICP-OES detection limits (Table 8). Fig. 9

summarizes the leaching test results for water-cooled slag. The W-20-0.5 slag was the sample with the lowest leaching with respect to the whole investigated samples. This trend is reflected again in the final pH values reached by the water after the test.

Since the addition of 20% by weight of silica coupled with water-cooling seems to be the best condition to assure the complete stability of the slag, a chemical sensitivity test was performed varying the initial pH solution from 5 to 12.5. Leaching test results as a function of initial solution pH were reported in Fig. 10. Leaching is significantly affected by the solution pH and during a leaching test the pH varies gradually, determining the dissolution phenomena of the different substances. The knowledge of the leaching behaviour of a material as a function of the environment pH could help to design the fate of such a waste when a beneficial use is considered. The investigated heavy metals (Ba, Zn, Pb, Cu and Cr) concentration, in solution of different pH, pointed out the typical trend for such a class of metals (Van der Sloot and Dijkstra, 2004). However, the test performed in neutral conditions high-lighted again the compliance with the Italian limit for the W-20-0.5 sample. Moreover this slag manifests an interesting capacity to neutralize both the acidic and the alkaline environment. In fact, the final pH of the exhaust solution reached

Table 8 – Results of standard leaching test (EN 12457-2) on as-received EAFD, alkaline (15% CaO) and acidic (15% SiO₂) reference Waelz slag, and laboratory modified slag (bold values overcome the limits listed in Table 2).

		Ba	Cu	Zn	Be	Co	Ni	V	As	Cd	Cr	Pb	Se	Hg	pH
EAFD	µg/l	1800	100	780	n.d.	n.d.	n.d.	40	n.d.	n.d.	150	870	n.d.	n.d.	8.5
<i>Reference Waelz slag</i>															
15% CaO	µg/l	500	10	300	n.d.	n.d.	n.d.	30	n.d.	n.d.	n.d.	300	n.d.	n.d.	10.3
15% SiO ₂	µg/l	200	n.d.	700	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.3
<i>Air-cooled Waelz slag</i>															
A-17.5-0.5	µg/l	280	35	440	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	50	n.d.	n.d.	7.81
A-17.5-2	µg/l	250	157	710	n.d.	n.d.	n.d.	25	n.d.	n.d.	75	110	n.d.	n.d.	7.86
A-20-0.5	µg/l	25	n.d.	285	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	32	n.d.	n.d.	7.62
A-22.5-0.5	µg/l	160	103	1160	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60	210	n.d.	n.d.	8.01
A-22.5-2	µg/l	130	80	830	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	75	120	n.d.	n.d.	7.91
<i>Water-cooled Waelz slag</i>															
W-17.5-0.5	µg/l	70	n.d.	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.77
W-20-0.5	µg/l	20	n.d.	115	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.58
W-22.5-0.5	µg/l	40	20	510	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	45	25	n.d.	n.d.	7.65

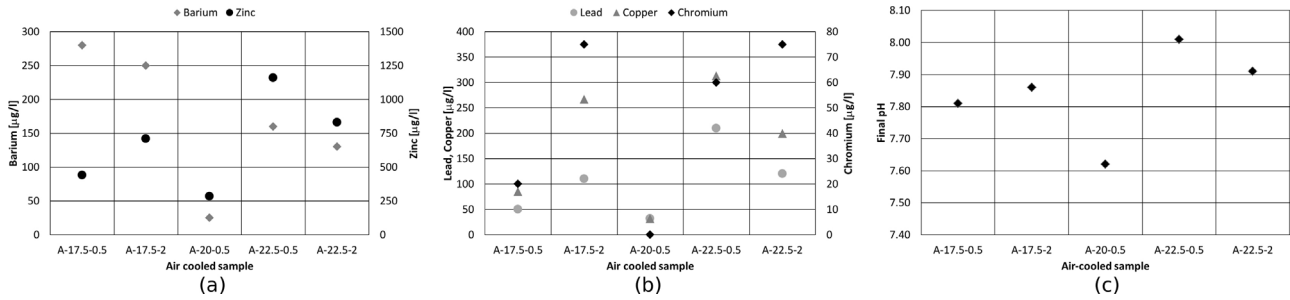


Fig. 8 – Results of standard leaching test (EN 12457-2) for air-cooled laboratory Waelz slag: (a) barium and zinc; (b) chromium, lead and copper; (c) final pH.

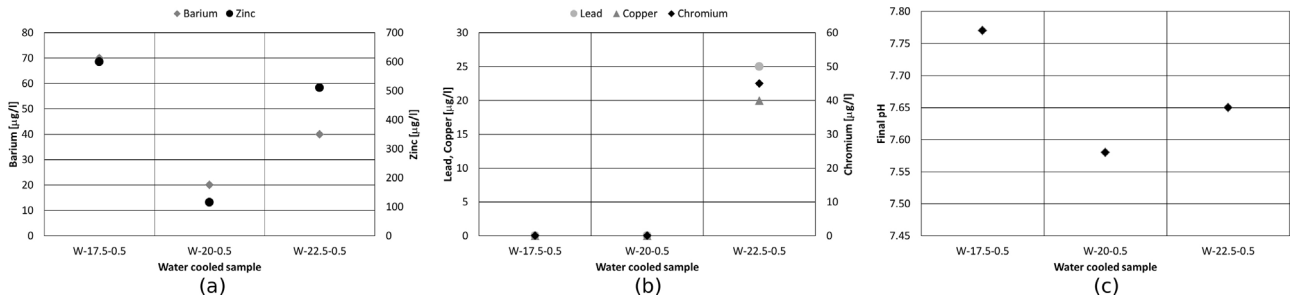


Fig. 9 – Results of standard leaching test (EN 12457-2) for water-cooled laboratory Waelz slag: (a) barium and zinc; (b) chromium, lead and copper; (c) final pH.

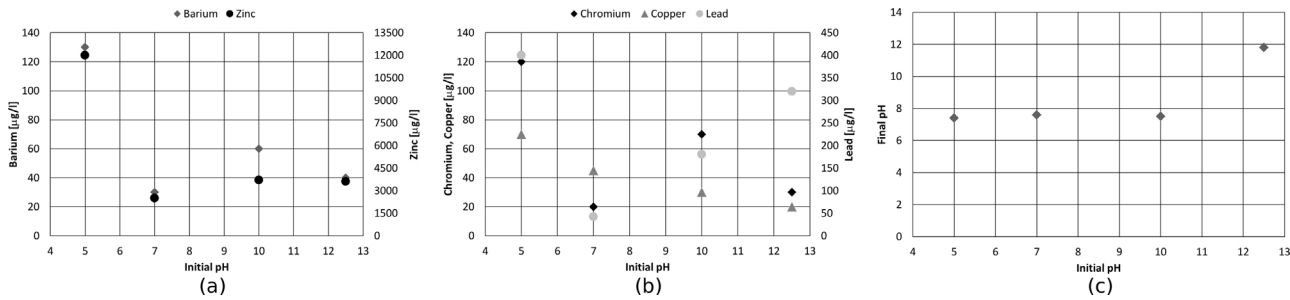


Fig. 10 – Results of pH-variable leaching test for 20% SiO_2 water-cooled laboratory Waelz slag: (a) barium and zinc; (b) chromium, lead and copper; (c) initial pH vs. final pH.

neutral values not only in standard environment (pH 7) but also at 5pH and 10pH. Even at 12.5pH the modified slag demonstrated also a good capacity to neutralize basic environment indeed the final pH reached a value about 11.5.

4. Discussion

On the basis of the leaching test results, the predominant factor in stabilization of the slag was definitely represented by the silica addition, which was necessary to form an amorphous matrix able to incorporate the crystalline phases. Moreover, the more acid the slag is the lower the release of barium, as previously indicated by Barella et al. (2012) and Mombelli et al. (2012, 2013). Although the natural olivines are unstable silicates when they come in contact with water and are very sensitive to weathering phenomena (Deer et al., 1994), in this specific case, their complex structure prevented their dissolution. Moreover, the glassy matrix helped keep the slag hydrophobic. Promoting pyroxenes formation, which are typically more stable than olivines (Deer et al., 1994), through a treatment time of more than 1 h appeared to be an incorrect practice. Even if the barium content was significantly decreased in the 2 h treated samples, the sulphides dissolution and the spinel growth increased the values of lead, copper,

zinc and chromium in the water solution. Copper and lead were mainly bound as sulphides, which are usually insoluble in water. The thermal treatment at 1300°C for longer than 1 h could induce disaggregation of sulphides that were dissolved in the glassy matrix under the form of oxides. These oxides were not fixed in the matrix and thus, they easily dissolved in the water. Zinc and chromium were instead aggregated within the formed spinels. The bigger the spinel size the higher the concentration of Cr and Zn in the water. The relative amount of both Cr and Zn inside the spinel determined their leaching. When the chromium concentration was high, the zinc was easily released and vice versa.

The leaching tests showed that the best condition to decrease heavy metals leaching is a treatment involving the addition of 20% of silica by weight to the slag and its water cooling. It is important to mention that in these experimental trials the effect of silica addition was studied only in an oxidizing atmosphere, thus simulating only the final part of the Waelz process. The final zinc and lead concentration in the slag will be lower than in the simulations due to a reduction reaction taking place in the middle section of the Waelz furnace. Thus, the quantity of these elements release after actual leaching will be considerably lower than during the experiments.

The chemical sensitivity at pH-variable test, carried out on this sample (W-20-0.5), shows a good neutralizing capacity of such a slag both in acidic and alkaline environment. In other words, this slag has an interesting buffer capacity at least in the range 5–10 pH. Thus, the exploitation of this slag as alternative raw material should be avoided in extreme acidic and high alkaline environment. However this slag demonstrated acceptable heavy metal leaching in the range 6–10 pH, and thus should be employed for less acidic environment neutralization or in less alkaline concrete production.

Moreover, the melting temperature reduction promoted by the addition of 20% of silica should contribute towards improving the efficiency of the Waelz process and increasing zinc extraction. The decrease of the melting temperature should decrease the consumption of coke and fuel, reducing the process costs. Actually, the mass is maintained in liquid form for more time, favouring a separation between iron and zinc oxide. In the second section of the rotary kiln, the reducing atmosphere could reduce a higher fraction of zinc, which would be transformed into Waelz oxide, increasing the process yield.

Then again, with an opportune set-up, it should be possible to produce liquid pig-iron from iron oxide reduction at the end of the rotary kiln.

5. Conclusions

This work has investigated the feasibility of Waelz slag inertization through a series of experiments designed to simulate the final part of the Waelz process. In particular, EAF dusts have been treated by adding different quantities of silica and varying the treatment time and cooling conditions.

On the basis of the experimental analysis, the simulated Waelz slag behaved according to the following key mechanisms:

- the silica addition facilitates a change in the structure of the powders dragged by the EAF fumes, transforming the calcium-rich phases into silicon–calcium–iron oxide ternary phases (olivines or pyroxenes) and promoting the formation of a glassy phase;
- the microstructural changes greatly reduce the concentration of heavy metals in the elute solutions;
- a further increase of the silica addition does not cause an unconditional improvement of the slag leaching behaviour;
- a long treatment time causes the dissolution of sulphides into the matrix and the Fe–Cr–Zn spinel agglomeration, but this process does not appreciably influence the slag stability;
- an increase in the cooling rate prevents the nucleation of calcium-silicate crystalline phases and reduces olivine growth, obtaining an amorphous structure with a low fraction of crystallinity;
- an increase in the cooling rate improves the slag leaching behaviour, decreasing the leaching of dangerous species.

The optimal combination of the studied variables appears to correspond to the application of these operative parameters:

- (1) addition of 20% of silica by weight;
- (2) the application of water cooling.

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