Spent Magnesia-Carbon Refractory Bricks from Steel Production: Potentiality of MgO-Clinker Recovery

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The work is focused on the quality of spent refractory materials (MC 98/10) from the slag line of steel ladles, which are freely dumped, and the effect of their dumping in a landfill on the environment. The degradability of the spent refractories in water is an indicator of their corrosion extent. The stability of corrosion products was evaluated by batch leaching test in water and weak acid medium (pH = 5.95 and 4.21; liquid: solid = 10). The conductivity and changes of pH in the medium were measured. Crushed new magnesia-carbon bricks increase the pH value of leachates to 9 – 9.5, the spent refractory from the core of the bricks generates pH = 10 – 10.5 and that of the material from the corroded surface of bricks shifts pH up to 12. The alkali ions (Na^+, K^+, Ca^{2+}) are eluted from the spent refractories. The increase of pH value to 11–12 leads to the saturation of solution with Ca^{2+}, Al^{3+} and sulphur ions, and to the stabilisation of heavy metals in the solid compounds. Because the MgO-clinker particles concentrate in the coarse-grained fraction the re-use of size fraction > 1 mm from spent MC 98/10 bricks as raw materials is hopeful. The recycling processes are being verified, and economic analysis is being prepared.

Key words: *leaching, pH value, magnesia refractory, redistribution, concentrate*

Introduction

The steel industry is a major consumer of a wide range of the refractory materials. Worn lining in ladles, basic oxygen furnaces and other furnaces is replaced permanently. As mentioned in the works (Malfliet et al., 2014; Fang et al., 1999), at the end of the 20th century, there were more than 3 million tonnes of refractories produced per year only in the USA and 80 thousand tonnes in the European Union. Statistics and technical works indicate that at present the steel industry recycles only a small part of spent refractory materials, approximately 1 − 10 %, mostly used as a slag conditioner or roadbed materials. Most of the spent refractory materials are freely dumped without previous treatment.

Pressure to improve the environmental sustainability and the growing price of virgin raw materials, force the operators to reduce the quantity of annually dumped spent refractories. For example, to increase the refractories quality and apply their prolonged use or recycling and also to reuse the spent refractories as raw material for new refractory or ceramics bricks (Malfliet et al., 2014; Hanagiri et al., 2008; Schutte, 2010; Nakamura et al., 1999; Kwong and Bennett, 2002).

On the one hand, the study of spent refractory properties helps to understand the corrosion processes under high temperature in the aggregates and their use in the production of the metal and refractory materials. On the other hand, the degree of the brick deterioration by the corrosion determines the options for their secondary utilisation. The works (Vadász et al., 1995; Arianpour et al., 2010; Conejo et al., 2006; Luz et al., 2013) are devoted to the pre-treatment and utilisation of spent refractories. Because the determining factor for the use of the corroded ceramic materials is their chemical and phase composition, each of the grain fractions of the crushed spent material must be analysed before its use into new ceramic masses (Malfliet et al., 2014; Hanagiri et al., 2008; Arianpour et al., 2010). The works (Fang et al., 1999; Arianpour et al., 2010; Othman and Nour, 2005) mention that a small part of crushed spent magnesia refractories can be added into new masses in the production of magnesia refractories and works (Conejo et al., 2006; Luz et al., 2013, Strubel e al., 2015) suggest their usage as a slag foaming conditioner.

This work deals with the spent magnesia-carbon (MgO-C) bricks the slag line of steel ladles. The magnesia-carbon unfired bricks are applied into the working linings of basic steel production units, electric arc furnaces, and of course for steel ladles slag lines, everywhere where the high resistance to molten metal and resistance to slag corrosion is required. These refractories are resisting to 1700 °C temperature and possess low wetting ability by liquid phase (STN EN ISO 10081, 2003). These bricks, containing up to 10 wt. % of carbon, are the optimal refractory material for the zone of the molten slag attack. The MgO-C bricks consist of sintered magnesia bound

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by resin. Depending on the application, the bricks can contain up to 98 wt. % MgO (periclase), and residual carbon from 7 to 30 wt.%. To prevent the burning up of carbon, the antioxidants are added to the refractory mass (Staroň and Tomšu, 2000).

The aim of the work was to define which elements of spent periclase-carbon bricks (MC 98/10) from the steel ladle lining are leached by water, to predict the impact of landfilling on the environment and to review the recycling possibilities of such spent refractories. For this reason, the samples were prepared from the surface and core of the corroded bricks that were leached separately in de-ionised water and a weak acid solution (pH = 4.21; simulating the acidic rain).

Materials and Methods

Materials

The sinter magnesia (min. 98 wt.% MgO; $\phi = 0 – 5$ mm) is the base of the MC 98/10 brick. Magnesia is combined with the organic bond which after burning creates approx. 9.5 wt.% of C. The tests were implemented with new and spent MC 98/10 refractory bricks coming from the lining of the steel ladle (after 95 runs of the casting).

The mortar from the bottom of spent bricks was easily removed before the preparation of the samples. One group of samples was prepared from the core of the spent bricks (mark KB), the second from the surface (mark KS), the removed corroded layer was approx. 20 mm thick. The reference grainy sample was prepared from new bricks (mark KN). These materials were crushed to the grain size < 2.5 mm. The specific surface (Quantachrome NOVA-1000; gas-N2 methods B.E.T.), magnetic ratio and loss on ignition (1000 °C/1 h) of grainy samples are shown in Table 1.

The results of classical soil chemical analysis of samples from surface and core (KB, KS) are shown in Table 2. The phase analysis was determined only for the samples from the brick core by XRD diffractometer (Rigaku MiniFlex 600), and the record (Fig. 1) was evaluated using the Quality Analysis software PDXL 2 and ICCD mineral and ceramics database.

Leaching test

Stability of the spent refractories in aqua medium was tested by batch leaching under the recommended conditions by Method of 1312 and Nordtest Report 539 (Method 1311, Method 1312; Baun et al., 2010). The samples were leached in de-ionised water (pH = 5.95 ± 0.05; conductivity $\sigma = 2$ μS.cm^{-1}; ORP (oxidation-reduction potential) = 100 mV) and/or in the weak acid solution (pH = 4.21 ± 0.05; $\sigma = 18$ μS.cm^{-1}; ORP = 245 mV). Acid solution was prepared from dilute solution of sulphuric acid/nitric acid mix (6/4 wt.). The pH value, conductivity and ORP were measured (Digital pH/ORP/D.O.Multi-9310) during the leaching in different times (1 – 120 h).

The batch tests were carried out with liquid-to-solid ratios (L/S) = 10 at the room temperature (t = 21 ± 2 °C). The liquid medium (50 ml) was added to 5 g dose of the dry sample of defined particle size fraction into the PE-bottles. The PE-bottles were stirred on rotator "Multi RS-60 biosan" at 15 rpm during tests. The tests were 3 – 5 times repeated and average values are shown in Tables 3,4 and Fig. 2. After filtration of the leachates, the concentrations of ions were measured by the inductively coupled plasma-atomic emission spectroscopy (ICP-AES/ iCAP 6000 Series).

Results

Characterisation of spent refractory

The corroded surface of a spent MC 98/10 bricks was rough, markedly corroded but without extensive metal deposits. The grainy black sample changed colour at ignition (Tab. 1). The losses on ignition point indirectly to the carbon content in the samples. The samples from brick core exhibited the higher loss on ignition. The magnetic proportion is very small (Tab. 1, 2).

The XDR pattern (Fig. 1) of the sample from spent brick core confirmed the dominant content of periclase (MgO) and graphite/carbon (C).

Tab. 1. The basic characteristic of samples from spent MC 98/10 bricks.

Sample	Mark	Magnetic ratio [wt. %]	Loss on ignition L.I. [wt. %]	Colour change after ignition	Specific surface area Sa [m²g⁻¹]
core	KB	≈ 0	10.18	black→ light grey	2.4
surface	KS	0.5 – 1.5	8.75	black → ochreous	1.8

Tab. 2. Chemical analysis of particle size fractions of spent MgO-C: KB – brick core; KS - corroded surface; L.I. - Loss on ignition.

Samples	Chemical analysis [wt. %]										
	Al_2O_3	SiO_2	MgO	CaO	Fe_2O_3	Na_2O	K_2O	SO_3	MnO	Cr_2O_3	L.I.
KB 0-2.5 mm	4.4	1.8	80.8	4.2	1.5	<0.05	<0.05	0	<0.25	0.1	9.2
KB 0-1 mm	6.5	3.2	72.1	2.8	0.9	-	-	-	-	-	11.2
KB 1-2.5 mm	3.8	2.1	83.4	1.6	1.8	-	-	-	-	-	7.0
KS 0-2.5 mm	5.6	1.4	62.6	19.7	1.5	0.15	<0.05	0	<0.25	0.9	8.2

The results of the chemical analysis of samples in Table 2 show the degree of the brick damage. The differences in the compositions between surface and brick core reflect the elements attacking the lining ladle in the area of the slag line. In the surface layer of spent brick (KS) the MgO content is reduced by about 20 wt.%. However, the content of CaO increased greatly, and that of Al_2O_3 increased only slightly. It is logical that the sinter magnesia cumulates in the coarser fraction (1-2.5 mm) and its concentration even increases after the carbon burns out.
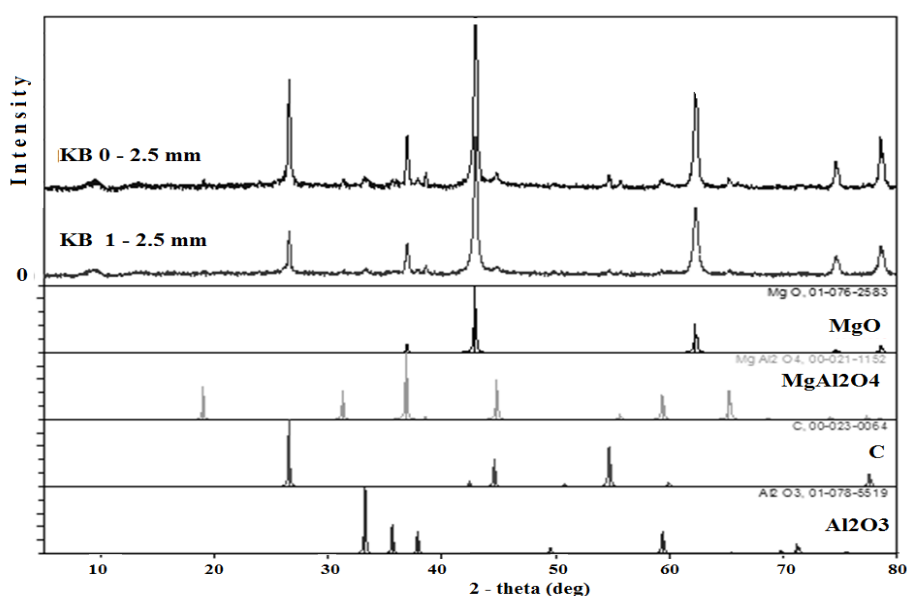

Fig. 1. XRD patterns of spent MC 98/10 from the brick core and diffraction lines of pure compounds.

Stability of MC 98/10 refractories and corrosion products in aqua medium

Prepared grainy samples from the spent MC 98/10 bricks for batch leaching tests were characterised by specific surface (Tab. 1). The fine carbon causes higher values of the specific surface of grainy samples.

One indicator of the degree of the corrosion of the material is the difference in extractability of the component. Conductivity grows with ion concentration of the solution, and the increased content of alkali ions (Na, K, Ca, Mg) shifts the pH value into the alkaline range.

Batch test with leaching medium replacement (medium – deionized water: pH = 5.95)

Fresh medium was carried out during the leaching of the KN, KB and KS samples during the time period of 1 h and 24 h. The pH value, conductivity and concentrations of major elements in solutions are listed in Table 3.

Although after the water renewal, the conductivity (σ) and concentration ions in leachates decreased, the pH values constantly increased. Material MC 98/10 itself belongs to the alkali refractories and creates the environment with pH = 9 − 9.5. There are not such significant differences between the sample of new material (KN) and sample from the core of spent brick (KB) as in the case of the samples from the core and surface of spent bricks (KB vs KS). Permanently high Ca^{2+}, Al^{3+} and sulphur content in the leachates points to the corrosion degree in the concrete parts of bricks. The results confirm that the corrosion of bricks was caused the alumina-calcareous slag and that sulphur, sodium and potassium elements attacking the surface penetrate into the brick core. The alkali and alkaline earth metals (Na, K, Ca, Mg) increase the alkalinity of leachates.

In addition to the elements listed in Table 3, also Pb, Cr, Zn and Cu elements have been measured, and their concentrations were on the detect-ability limit (0 − 0.02 mg.l^{-1}).

Tab. 3. Comparison of concentration, pH value and conductivity of leachates from new and spent MC98/10 bricks; leaching medium was changed after 1 h and 24 h (initial pH –5.95).

Sample/ Leaching time		Concentration of elements in leachate [mg.l⁻¹]								pH (± 0.2)	Conductivityσ [μS.cm⁻¹]
		Al^{3+}	Si^{4+}	Mg^{2+}	Ca^{2+}	$Fe^{2+/3+}$	Na^+	K^+	S-ions		
KN	1 h	11.7	0.75	5.15	8.56	0.01	1.50	0.17	0.35	9.50	95
	1-24 h	12.8	0.12	1.98	14.9	0.00	0.77	0.21	0.05	9.58	92
	24-48 h	12.1	0.10	0..89	13.1	0.00	0.45	0.20	0.00	9.35	79
KB	1 h	28.7	1.02	3.10	31.3	0.13	4.09	7.20	2.90	10.00	197
	1-24 h	86.8	1.02	2.16	50.5	0.05	1.18	1.77	1.65	10.17	255
	24-48 h	41.1	0.70	1.95	29.2	0.05	0.00	0.65	0.86	9.94	169
KS	1 h	370	2.23	0.66	232	0.02	5.47	4.20	2.90	11.88	1572
	1-24 h	247	1.77	0.34	176	0.03	4.60	1.00	2.34	11.69	1335
	24-48 h	210	2.17	2.14	187	0.05	1.71	0.48	2.70	11.80	1412

One-stage batch leaching test in mediums of deionised water and weak acid water

The results of the leaching without exchange of mediums, deionised water and weak acid solution, are presented in Table 4 and Fig. 2. Of course, the character of periclase-carbon refractories eliminates acidity of medium immediately and shifts the pH into the alkaline region. Therefore the results of leaching in water (pH = 5.95) and weak acid solution (pH = 4.21) are similar; the ion concentrations are only a bit higher in leachates of the weak acid solution than in water. The increasing conductivity is in correlation with the increasing concentrations of ions in the solution.
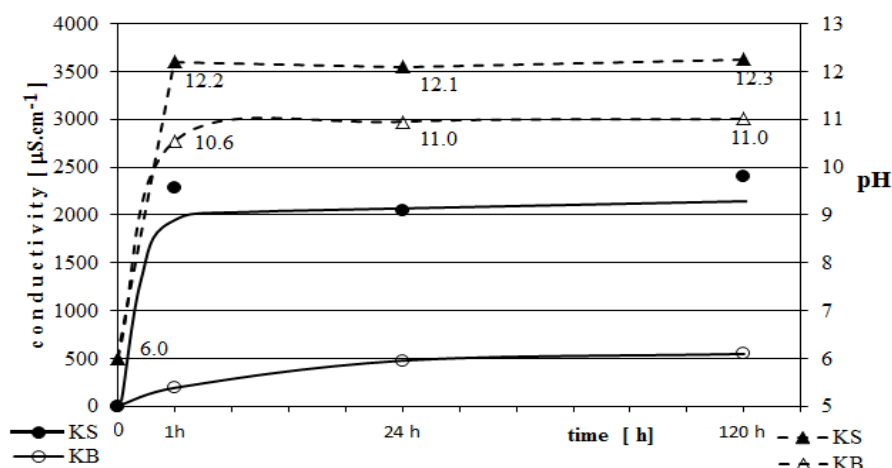

Fig. 2. Changes of conductivity and pH in leachates with leaching time of spent MC 98/10 refractories in water: batch test without change of leaching medium – initial pH = 5.95; KS – sample from the surface; KB – sample from the core of brick.

Comparing the test results with and without replacement of leaching mediums indicates a supersaturation of solution already during the first hour of leaching in case of the sample from surface bricks.

In addition to elements presented in Table 4, the contents of Pb, Cr, Zn, and Cu ions were also measured. Only Zn was detected in concentration max. to 0.15 mg.l⁻¹ in leachates and the others monitored heavy metal ions were not detectable.

Tab. 4. Concentration of ions in leachates after 24 h of leaching of spent MC 98/10 in water – W (initial pH = 5.95) and acid solution – A (initial pH = 4.21; sulphur in initial acid solution = 0.5 mg.l⁻¹).

Samples	Concentration of elements in leachates [mg.l⁻¹]								pH (± 0.2)	Conductivity σ [μS.cm⁻¹]
	Al^{3+}	Si^{4+}	Mg^{2+}	Ca^{2+}	$Fe^{2+/3+}$	Na^+	K^+	S-ions		
KB /W	115	1.89	0.87	78.8	0.04	4.98	7.85	2.36	11.0	480
KB / A	99.0	1.52	2.34	80.7	0.07	6.12	10.9	3.33	10.5	345
KS /W	265	2.40	0.28	208	0.01	9.36	5.20	3.60	12.2	2005
KS / A	294	2.36	0.63	257	0.02	14.0	10.1	2.83	12.0	1836

It is also necessary to mention that spent MC98/10 samples changed initial pH = 1 of leaching medium (H_2SO_4 + HNO_3) to 9.1 − 9.5 during 1 hour of the leaching and no leachates contained detectable amounts of Pb, Fe, Cr, Zn, and Cu (concentration above 0.01 mg.l⁻¹).

Differences in composition of coarse and fine particle size of the sample from the spent brick core
(medium – acid water: pH = 4.21)

The weight ratio of the 0-1 mm and 1-2.5 mm grain size fractions in the crushed samples (0-2.5 mm) was 50 – 60 wt. %: 40 – 50 wt.%. As shown in Table 2, the coarser fraction (1-2.5 mm) contains more MgO and less CaO, SiO_2, Al_2O_3. The value of loss on ignition suggests the carbon presence and that its content is lower in comparison to the finer fraction. The results of phase analyses as well as confirmed it as well (Tab. 5).

Tab. 5. X-ray analysis results from the brick core of spent MC 98/10.

Phase	Content [wt.%]			
	KB 0-2.5 mm		KB 1- 2.5 mm	
Periclase (MgO)	80 – 87	<	88 – 91	
Graphite (C)	5 – 10	>	2 – 4	
Spinel ($MgAl_2O_4$)+ Corundum (Al_2O_3)	11 – 6	>	(4 – 6)	

The results obtained at leaching of ⟨0-1⟩ mm and ⟨1-2.5⟩ mm grain size fractions if medium (weak acid; initial pH = 4.21) was replaced in different time intervals are shown in Table 6.

Tab. 6. Concentration of ions in leachates from brick core (KB) and surface (KS) at the end of leaching cycles; replacement of medium - weak acid solution (pH = 4.21; content of S in initial solution = 0.5 mg.l^{-1}).

Samples / Leaching time	Concentration of elements in leachates [mg.l^{-1}]							
	Al^{3+}	Si^{4+}	Mg^{2+}	Ca^{2+}	Na^+	K^+	S-ions	pH
KB 0-1 mm/ 1h	20.8	1.17	1.97	46.2	9.00	10.4	7.64	10.05
KB 0-1 mm/ 1-24h	41.3	1.57	0.58	92.4	2.22	2.16	3.91	10.80
KB 1-2.5 mm/1h	11.2	1.54	3.55	24.6	4.71	4.57	3.57	9.80
KB 1-2.5 mm/1-24h	26.3	1.14	0.75	71.5	1.72	1.47	2.11	10.75
KS 0-1 mm/ 1h	253	3.54	0.13	339	11.1	4.50	5.21	12.25
KS 0-1 mm/ 1-2h	236	3.38	0.31	323	4.51	1..16	4.61	12.10
KS 0-1 mm/ 2-24h	224	3.09	0.50	295	3.90	0.57	4.31	12.15
KS 1-2.5 mm/ 1h	135	2.22	0.70	209	4.00	1.66	4.50	12.00
KS 1-2.5 mm/ 1-2h	154	2.26	0.36	213	2.52	0.41	3.69	11.95
KS 1-2.5 mm/ 2-24h	213	3.23	0.86	301	3.60	0.66	4.29	12.15

The pH values of leachates from the different grainy samples are similar. After each replacement of the medium, the pH value returns to the alkaline region rapidly. In case of the KB samples the pH increased up to 10 – 10.5 for 1 hour of leaching and in case of KS sample even up to 12, and with the exposure time, the pH practically did not change. Unlike the pH value, there are marked differences between the conductivity of leachates from the fine and coarse fraction. The conductivity corresponds to ions concentration in leachates. The leachates from the brick surface contain 5 to 10 times higher concentrations of Ca^{2+}, Al^{3+}, Si^{4+} than from the brick core. However, the Na^+, K^+ and sulphur contents are comparable. Among the heavy metals (Pb, Zn, Fe, Cr, Cu) only Fe and Zn have been detectable, and their concentrations were under 0.08 mg.l^{-1}.

Discussion

The behaviour of spent magnesia-carbon refractory in a landfill
The results of this study, the chemical analysis of MC 98/10 samples prepared from the core and surface of corroded refractory bricks (Tab. 2) and analyses of leachates (Tab. 3,4,6), confirmed that the refractories do not belong to the hazardous waste group.

Unused magnesia refractories create an alkaline environment (pH 9.5). In case of the leaching of crushed spent brick in a small quantity of the liquid, the pH can rise to 12. Major extractive elements, Ca^{3+}, Al^{3+} and sulphur, come from slag. At the beginning of the leaching process, the Na^+ and K^+ ions elute very intensively because Na$^-$ and K$^-$compounds are less stable in water. The continuous extraction of Ca^{2+} from spent refractory causes the constant shift of the pH value to the alkaline region (pH = 10 - 11).

The alkaline medium is highly corrosive to silicates and alumina-silicates though it prevents the dissolution of heavy metals. This means that the slag and corrosion compounds (Ca-Al-Si-O) are attacked. The shift of pH to alkaline region causes the gradual dissolving of Al-precipitate and increases the amount of $Al(OH)_4$/AlO_2^- ions in the solution (Jenny, 1980). This explains the higher Al concentration in the leachate at pH > 10.

The $Fe^{2+/3+}$, Pb^{2+}, Cr^{3+}, Cu^{2+} and Zn^{2+} concentrations are very low in alkaline leachates (pH = 9 – 10). The work (Monhemius, 1977) dealing with the solubility of metal hydroxide explain the conditions under which heavy metals will not be released in the aqueous medium. The ion concentrations in the aqueous solution depend

on the pH values as well as the electrode potential, which create all components of the solution. The measured values of the redox potential of the leachates were within the range of -80 to 10 mV (t = 20 °C). For measured ion concentrations (Al = 270 mg.l^{-1}; Ca = 400 mg.l^{-1}, Si = 2.8 mg.l^{-1}, S = 3.2 mg.l^{-1} and Mg = 0.25 mg.l^{-1}) the Eh-pH diagram in the region of pH = 10 – 12 and E = −80 - +10 mV, predicates the following condensed phases: calcium-alumina-silicate-hydrate and gypsum [calculated by HSC/(Roine et al., 2011)]. If the leaching media are not changed continuously, then the saturation and precipitation occur. The spent MC bricks in the landfill have a similar influence on the heavy metals ions sorption as cement and concrete which are also an alkaline character (Kozáková et al., 2013, Plešingerová et al., 2015). The precipitation processes are very difficult and are affected greatly by the weather change in the landfills.

Spend refractory as secondary raw-materials

The main purpose of the recycling of the spent refractories is to recover a secondary raw material and minimise the landfills. Generally said, the recovered secondary raw materials are of the lower quality. For the recycling of the spent refractories, the most corroded parts of bricks must be mechanically separated in the stage of the lining demolishing.

From tested spent MC 98/10 bricks the enriched fraction (particle size > 1 mm) by sinter MgO can be obtained by disintegration and size separation (Tab. 2). The phase and chemical composition of the brick core are in correlation with the original refractory material. Carbon and alkali enrich fine fraction.

Leaching tests of magnesia-carbon refractories carried out in an aqueous medium pointed at the extent of the corrosion on the surface and in the core of bricks. The leaching amounts of Na$^+$, K$^+$ and S-ions from the surface and core are relatively low (Tab. 6). That confirms the intense diffusion of alkali and sulphur ions into bricks. Recovery of the secondary raw materials is dependent on the content of Na, K, Ca and Fe substances. The concentration of Na$^+$ and K$^+$ in the fraction class 1 – 2,5 mm of spent refractory are low (Tab. 2).

Recycling of sinter magnesia from spent MC 98/10 requires *i)* to remove mortar from the bottom part and the more corroded top surface of bricks (CaO content in leachates from the corroded surface is 5 times higher than from core); *ii)* to disintegrate and separate coarse fraction (particle size > 1 mm). Even if a magnetic part in debris is small, the magnetic separation is necessary. Burning of the material, which will remove carbon and this should increase the MgO content up to 90 – 93 wt.% in (1-2.5) mm fraction (Tab. 5). The phase and chemical composition, thermal stability, size and shape of particles, will determine the use of fractions.

The results mentioned above can serve as a starting point in searching for the utilisation of the spent MC 98/10 bricks as secondary raw material. The use of spent refractories depends on the processing cost and quality of the recovered coarse fractions.

Conclusion

Tested MC 89/10 lining from steel ladle was corroded by slag. On the strongly corroded surface of bricks, the content of Ca and Al compounds is higher, but there is the only small amount of magnetic components. The Na, K and sulphur are present in hundredths of wt.% only. The surface layer is difficult to separate from the less corroded brick core.

Magnesia-carbon refractories (MC 89/10) create the leachates with pH = 9 – 9.5. The corrosion of the slag accelerates leachability of corrosive compounds, what causes an increase of pH up to 12, independently of initial pH (4.21 – 5.95) of leaching medium. The content of extracted Ca^{2+} ions into water causes increasing of pH value. In addition to Ca^{2+}, sulphur, Al^{3+}, Na$^+$, K$^+$, less Si^{4+} and Mg^{2+} are leached. Ions of Na$^+$ and K$^+$, which are present in the surface layer and also in the core, are partially washable. The tendency to move and maintain pH in the alkaline region inhibits dissolving of the heavy metals from compounds. If the leaching medium is not continually renewed, then it becomes quickly saturated with Al^{3+}, Ca^{2+}, Mg^{2+} and Si^{4+} ions.

The C-content and impurities in the spent magnesia refractories predetermine debris to their use for the decontamination of the acid soils/water. This method of processing is not costly, but a portion of refractory materials is lost. It will be necessary to recycle material from MC bricks for recovery of MgO clinkers in the future. The recovery of the coarse fractions enriched by MgO-clinker (90 wt.%) requires the purification, i.e. disintegration, separation of coarse fraction, washing out and burning. The utilisation of the fine and dusty fractions as an additive to the slags depends on their physical and chemical properties.

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