# ZEWA (Zero waste) process: a new way for co-processing steel slag

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**Abstract**
This paper summarizes the results obtained in the frame of an European project involving eight partners from steel, coal and cement industry.
Its objective is to set up a process to transform by products generated from the major industrial sectors into valuable mineral and metallic products enabling a reduction of $CO_2$ emissions. The by products are steel slags, residues from scrap conditioning and car dismantling, fly ash from power plants and bottom ash from municipal incinerators. A pilot plant was erected at Vitkovice steelworks (Ostrava CZ) and 11 campaigns have been performed.
The feasibility of the process and the suitability of the various by products have been assessed. The mineral and metallic products have been fully characterized. All mineral samples were chemically and mineralogical analyzed and submitted to the grinding test, reactivity test, leachability test for soluble chromium evaluation. All these test indicate that the synthetic slags obtained from the ZEWA process are not fundamentally different from an industrial granulated blast furnace slag and there would appear to be no technical obstacles to their use as additions to Portland cement clinker after obtaining a technical agreement from the official institutes.

*Keywords* : steel slag, blast furnace slags, fly ash, reactivity index, $CO_{2,}$ electric arc furnace


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## 1. Introduction

The objective of the ZEWA ( ZEro WAste ) project is to find a new metallurgical route for the on line conversion of by-products into valuable mineral and metallic products with a reduction of $CO_2$ emission. Fundings were provided at 50% by the European Community (reference G5RD-CT-2000 00307, 5 Frame work Programme)

The by-products, generated in large quantities by the major industrial sectors are: steelmaking slags, residues from scrap conditioning and car dismantling, fly ash from power plants, bottom ash from urban incinerators.

This project was divided in 4 steps: the choice of the technology of treatment, the organisation of the partnership, the pilot plant trials and the analysis of the resulting products.

Many publications and patents have been published during this project [1-6]

In this paper, we summarize shortly the different steps with the corresponding references of published papers and patents and we focus our attention on the results concerning the hydraulic binder obtained during the pilot plant trial at Vitkovice.

## 2. Description of the project

### 2.1 Choice of the technology

Among the different routes to process steel slags two have been specially studied. Liquid slag can be oxidised by oxygen injection [7] , $Fe^{++}$ oxidised into $Fe^{+++}$ that combines with free lime to give calcium ferrite. Industrial application developed by Thyssen produces a sound aggregates [8]. Laboratory experiments show that it is also possible to obtain an hydraulic binder. In this process, the metals (Fe, Mn, Cr, Ni, ) remain in the mineral phase and are not recovered [9-10]. That contributes to a deficiency in the economic balance of the process. In addition, this process treat only steel slags and cannot be adapted to the treatment of sludge, dust…..

We select a treatment under reducing conditions, originally described in the reference [11]. Steel slags, sludges, dusts are treated at liquid state by a reducing agent which can be carbon based compound, but also aluminium or ferrosilicon, depending on the level of reduction that can be achieved. During this reduction, the chemical composition of the slag is adjusted by adding silica or alumina bearing mineral. These products can also be by products from other industries (car dismantling, fly ash, bottom ash from municipal incinerators). At the end of the heat, we obtain a metallic product containing Fe, Mn , Cr, … and a mineral product whose chemical composition is close to that of industrial blast furnace slag. The principle of this reduction treatment is known and technologists have tried to apply it industrially. Among these numerous processes the Inmetco direct reduction process deserves more attention [12]. It comprises several processing stages i.e. production of green pellets,


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direct reduction in a rotary hearth furnace and finally melting in a submerged arc hot-metal melting furnace. In the ZEWA process, we only use an electric arc furnace. This engineering aspect of the project has been described in patents and publications [4-5]

### 2.2 Partnership

Eight partners were involved in this project

VOEST ALPINE INDUSTREANLAGENBAU GMH1& Co ( Presently SIEMENS) was in charge of the engineering

Three steel companies represent the main steelmaking route: the blast furnace ( USINOR, presently MITAL) the electric arc furnace for high carbon steel (Profil ARBED research center presently MITAL), and the production of alloyed steel ( ALZ, presently MITAL)

INSTITUT FOR CHEMICAL PROCESSING OF COAL supplies the reducing elements

COMET SAMBRE S.A , suppliers of car dismantling residues

LAFARGE was in charge of evaluating the final products.

CRM Centre de recherche métallurgique ( Belgium) was in charge of coordination

### 2.3 Pilot plant trials

An electric arc furnace (12 MVA) has been erected in the foundry of Vitcovice Steelworks in Ostrava, in order to use the available power supply and the fume extraction system.

The inner dimension of the ladle are 2,25 m average, diameter and 2,8 m height . During the pilot plants experiments, it hold 15 tonnes of hot metal and 3 to 5 tons of slags out of which approximatively 200 kg were quenched in order to obtain an average of 85% glass in the slag. The test programme includes 11 campaigns with 70 heats.

### 2.4 Analysis of the final mineral products.

The chemical target of the slag was chosen according to the published literature and specially the results obtained by Locher [13]

Figure 1 represents the phase diagram $CaO\text{-}Al_2O_3\text{-} SiO_2$ [14] and the zone defined by Locher showing the area of chemical composition giving different range of strength. The upper green zone was our targeted chemical composition.

Table 1 gives the average chemical compositions and the % of glass of the ZEWA slags as well as the range of variations.

The dots representing the chemical composition of the ZEWA slags have been plotted on the diagram in figure 1.

We see that points are scattered around the targeted zone. This can be explained because during the trials, we have extended the experimental conditions in order to cope with the variability of the industrial waste. As a consequence the chemical composition targeted was only approximately attained but this could give interesting information.


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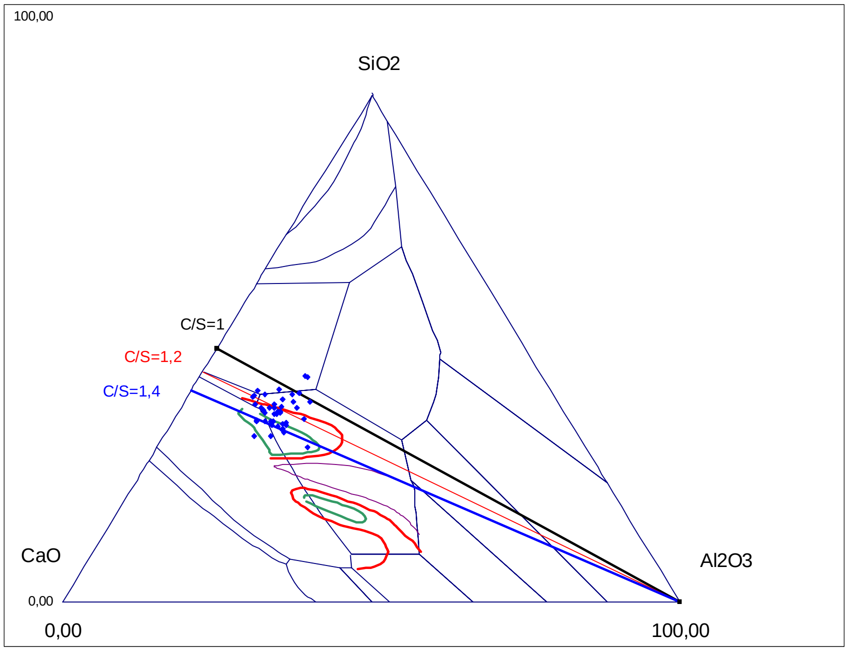
Figure 1
Position of the chemical compositions of the ZEWA slags
in the diagram CaO- $Al_2O_3$- $SiO_2$




The positive effect of the $Al_2O_3$ content up to 15% has been recognised by many authors. From Wang et al [15], $Al_2O_3$ content should be no lower than 10,5% and the CaO no lower than 40%. We tried to obtain an average of 13% of $Al_2O_3$ content in the ZEWA slags.

The mineralogical composition was defined to reach 85% of glass according to the European Standard for the BF slag

Table 1
Average chemical composition of the ZEWA slags

| Oxides | SiO2 | Al2O3 | Fe2O3 | FeO | CaO | MgO | K2O | Na2O |
|---|---|---|---|---|---|---|---|---|
| Average | 31,35 | 13,52 | 0,57 | 0,98 | 39,54 | 9,45 | 0,35 | 0,21 |
| minimum | 25,46 | 9,00 | 0,00 | 0,00 | 30,40 | 6,30 | 0,00 | 0,00 |
| maximum | 35,00 | 21,2 | 3,17 | 4,29 | 43,40 | 13,12 | 0,80 | 0,33 |
| Oxides | SO3 | TiO2 | Mn2O3 | P2O5 | Cr2O3 | ZrO2 | SrO | Glass |
| Average | 0,29 | 1,15 | 2,26 | 0,14 | 0,75 | 0,02 | 0,02 | 87 |
| minimum | 0,00 | 0,46 | 0,20 | 0,00 | 0,00 | 0,00 | 0,00 | 67 |
| maximum | 0,52 | 1,61 | 5,40 | 0,77 | 1,64 | 0,04 | 0,04 | 99 |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The most important question to answer is whether or not ZEWA slags can be considered to fall within the normal range of compositions of conventional blast furnace slags. Since we can only with great difficulty account on a scientific basis for many of the differences between blast furnace slags from different sources, it is unreasonable to expect us to account for differences between these ZEWA slags compositions (chemical or mineralogical) and blast furnace slags unless they are clearly extremely different which does not appear to be the case. The success of this type of project depends on the addition of several advantages compensating the extra cost for the treatment. Among them the recovery of the metal, prevention of the landfill of waste,$CO_2$ and natural resources savings. Apart from the economic issue that is out of the scope of this paper, it is necessary to sort out the main technical and industrial points in order to answer to the question: can the present results contributes to general knowledge of the hydraulicity of BF slags?

### 2.5 Properties of the ZEWA Slags

Slags produced by the ZEWA process are similar to industrial blast furnace (BF) slags by their chemical and mineralogical composition, but they cannot be standardized as BF slags because they are not produced by a blast furnace but by an electric furnace.

It was thus necessary to prove that they behave like usual cementitious additives for example industrial BF slag. Many experiments have been carried out to confirm their properties. They concern mainly the reactivity index, (according to the standard ASTM C 989-97 b), the deleterious elements leaching (according to the standard EN 12457-2 ), sulphate attack, freeze thaws resistances and carbonation. The results concerning the durability are quite positive and have been published elsewhere [16]. This paper deals only with the results obtained by the reactivity index measurement.

## 3. Experimental procedures

The slags have been ground down to fineness of 400$m^2$ /kg and mixed with Portland cement CMI ( 50%) . Mortar has been prepared according to the European standard (prism of 4x4x16 cm) and compressive strengths are measured at 1, 2, 7, 28 days. Reactivity index (RI) is then measured as the ratio between the strength of the slag cement over the strength of the pure Portland cement (We thus obtain RI 1 day, RI 2 days, RI 7 days and RI 28 days)

## 4. Results

The slags have been classified according to their RI 28 days, from 50 to 60, 60 to 70, 70 to 80, 80 to,90, 90 to 100 and higher than 100; Table 2 gives the chemical composition and the % of glass of the class of products in the range of RI 28.

At the bottom of the table 2 the potential mineral composition of the ZEWA slags, is indicated, assuming a total crystallisation calculated from the solidus of the phase diagram $CaO-Al_2O_3-SiO_2-MgO$. Figure 2 gives the variation of reactivity index with time. It can be seen that


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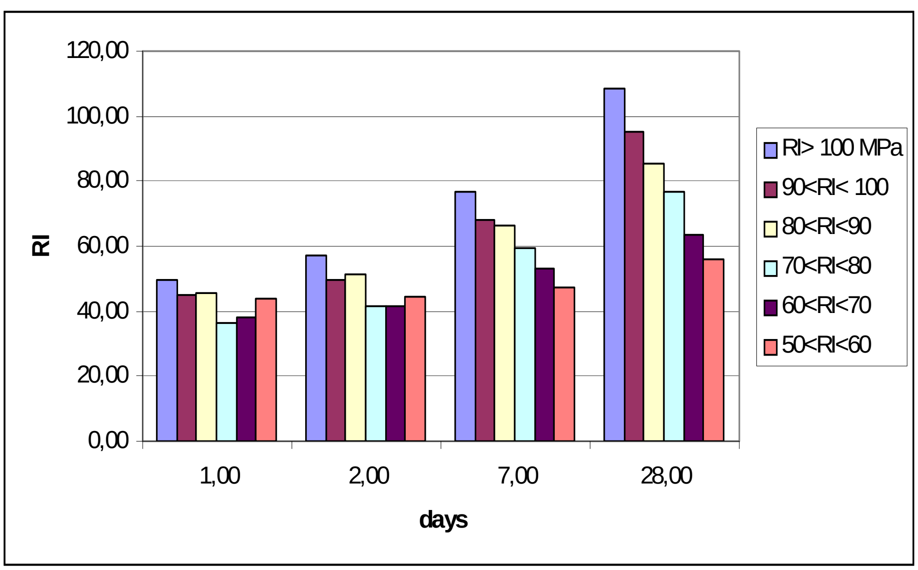
the sequence is the same for 7 and 28 days. The range of RI becomes smaller at 2 and specially at 1 day

Table 2
Chemical composition of the ZEWA slags according to their reactivity index

| Average R28 | >100 | 90/100 | 80/90 | 70/80 | 60/70 | 50/60 |
|---|---|---|---|---|---|---|
| SiO2 | 31,29 | 32,43 | 31,70 | 32,62 | 31,67 | 30,38 |
| Al2O3 | 13,50 | 13,91 | 13,05 | 14,29 | 13,50 | 11,10 |
| Fe2O3 | 0,43 | 0,37 | 0,02 | 0,19 | 1,45 | 1,16 |
| FeO | 0,84 | 0,67 | 1,16 | 0,63 | 0,87 | 2,50 |
| CaO | 40,61 | 39,93 | 39,88 | 38,64 | 37,30 | 34,48 |
| MgO | 9,65 | 9,00 | 10,01 | 9,72 | 8,89 | 11,46 |
| K2O | 0,35 | 0,36 | 0,33 | 0,27 | 0,42 | 0,26 |
| Na2O | 0,18 | 0,19 | 0,20 | 0,18 | 0,24 | 0,27 |
| SO3 tt | 0,29 | 0,32 | 0,26 | 0,28 | 0,25 | 0,17 |
| TiO2 | 1,17 | 1,11 | 1,23 | 1,23 | 1,17 | 1,21 |
| Mn2O3 | 1,48 | 1,77 | 1,98 | 1,90 | 3,66 | 2,75 |
| P2O5 | 0,05 | 0,04 | 0,12 | 0,05 | 0,36 | 0,01 |
| Cr2O3 | 0,57 | 0,71 | 0,26 | 0,68 | 1,14 | 4,79 |
| ZrO2 | 0,03 | 0,01 | 0,03 | 0,02 | 0,02 | 0,03 |
| SrO | 0,02 | 0,02 | 0,02 | 0,03 | 0,02 | 0,01 |
| LOI | -0,42 | -0,36 | -0,29 | -0,26 | -0,65 | -0,49 |
| total | 100,03 | 100,50 | 99,97 | 100,45 | 100,31 | 100,08 |
| C/S | 1,30 | 1,23 | 1,26 | 1,20 | 1,20 | 1,13 |
| %Glass | 94,91 | 95,33 | 89,60 | 88,50 | 85,24 | 91,75 |
| Mellilite | 57,06 | 76,16 | 60,69 | 80,40 | 81,81 | 59,86 |
| CMS | 14,56 | 7,18 | 15,60 | 12,84 | 7,61 | 27,34 |
| C3MS2 | 23,41 | 11,92 | 18,32 | 2,02 | 1,93 | 0,20 |

Figure 2
Reactivity index versus time



## 5. Discussion

### 5.1 Effect of the chemical compositions:

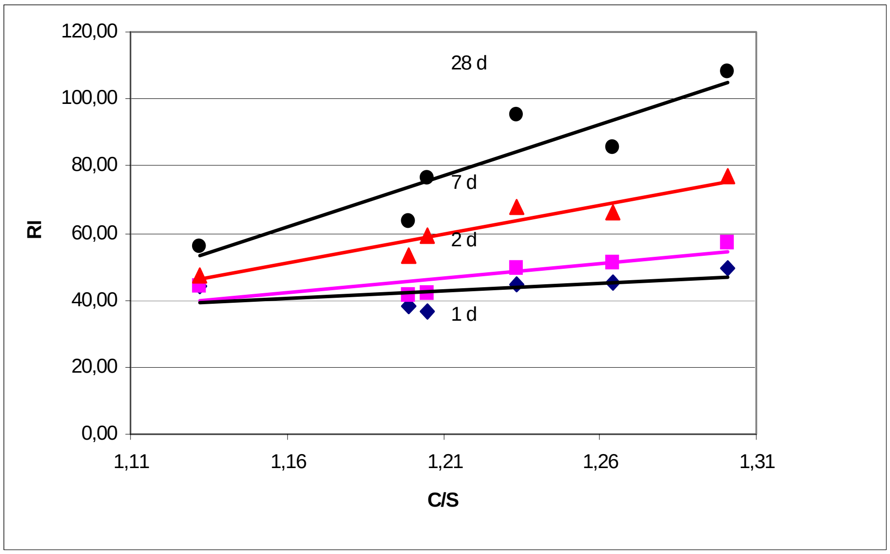
Many attempts have been done to correlate of the properties of the BF slags ( specially the strengths) to their chemical composition, using indexes and ratios[17] . Some of them involved the main oxide CaO, $SiO_2$ and $Al_2O_3$ or MgO with the ambiguity to locate MgO and $Al_2O_3$ at the denominator or numerator:CaO/SiO2, CaO/$Al_2O_3$, (CaO+ MgO)/$SiO_2$, (CaO+MgO+ $Al_2O_3$) / $SiO_2$, (20+ CaO+ $Al_2O_3$+0,5MgO-2 $SiO_2$ )

Some other involved the elements present in small quantity such as MnO or $TiO_2$ example $SiO_2$/( $Al_2O_3$+ $Fe_2O_3$+MnO+$TiO_2$).

In the present case, the best results were obtained from the simple basicity ratio CaO/ $SiO_2$ ( figure 3) at 7 and 28 days with a correlation coefficients of 0,84 and 0,91. At 1 and 2 days, the variation is too small to allow a significant correlation.

Figure 3

Reactivity index versus CaO/SiO2 for ZEWA slags




### 5.2 Effect of minor elements

The reason for the poor correlation between the chemical composition represented by the main oxide and the reactivity index was researched by the influence of minor elements [18-19]. Statistics treatments point out the influence of $TiO_2$,$Na_2O$, $F^-$ and $Cl^-$. . in the present case, the best correlation was found with Mn++ ( correlation coefficients 0,94, 0,92 at 7 and 28 days). The results at 28 days do not agree with the findings of Demoulian and al. [19] which indicates a positive effect of $Mn^{++}$ at 28 days.


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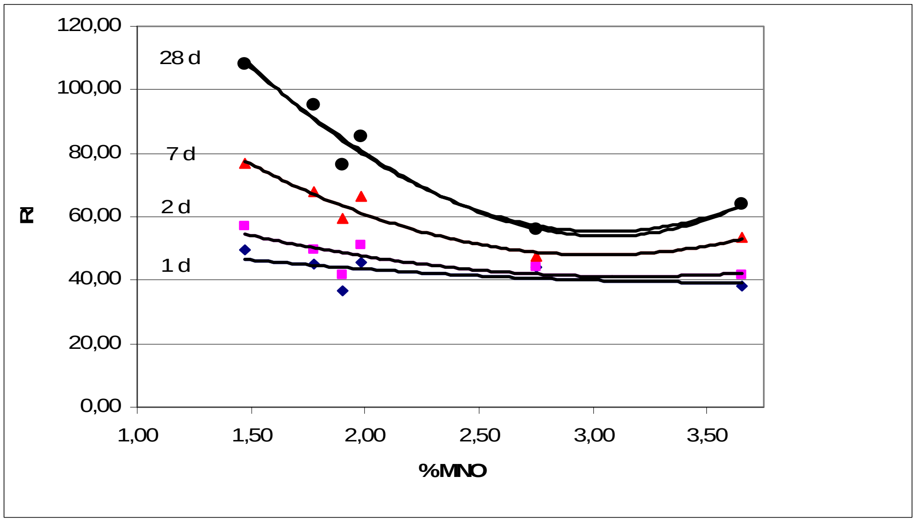
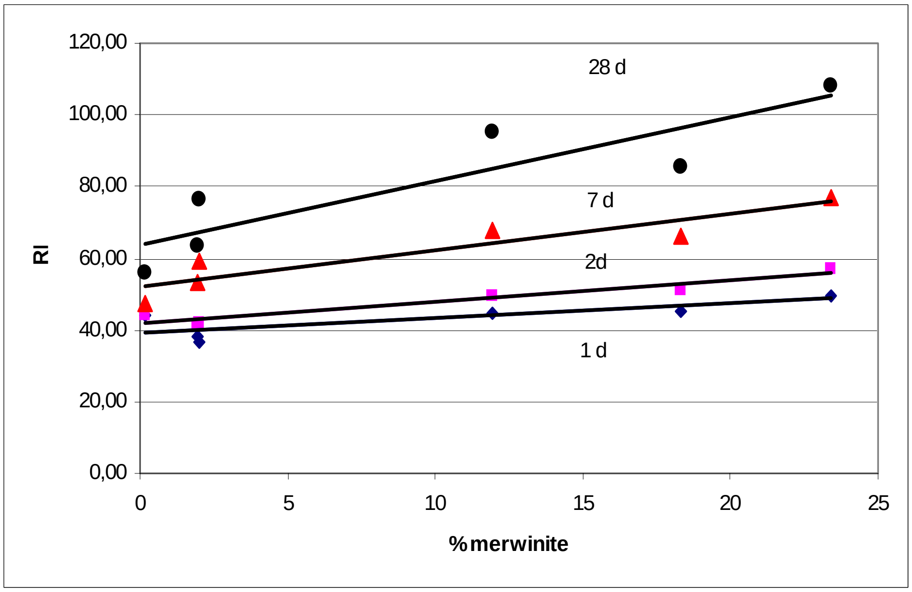
Figure 4
Influence of Mn++ on the RI of ZEWA slags




## 5.3 Effet of mineralogy

Figure 5 shows the influence of the amount of merwinite, calculated from the solidus of the diagram CaO-$Al_2O_3$, MgO-$SiO_2$ and the reactivity index RI

Figure 5
Influence of the calculated content of merwinite and the RI of ZEWA slags





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It is known that the BF slag is more reactive when in the glassy stage [20] On the other hand, Demoulian et al [19] indicate that a separation of up to 5 % of merwinite crystal has a beneficial effect on the strengths development due to the increase of alumina content of the glassy phase.The cristallisation of merwinite as primary phase leads to increasing reactivity whereas melilite diminished reactivity Some other researchers claim that the devitrification products can be regarded as indicator of the reactivity. Wang et al [21] find a good correlation between the melilite content (solid solution of gehlenite and akermanite ) and slag reactivity. They conclude that a close relation ship exist between the structural parameters of melilite and slag reactivity.

In the present study we have calculated the percentages of phases assuming a total cristallisation. Figure 5 shows a reasonably good correlation between the calculated content of merwinite and the RI (correlation of 0,8, 0,85, 0,9 and 0,6 at 28, 7, 2, 1 day). This correlation is not totally surprising because the precipitation of merwinite occurs when C/S > 1 (around) and we have seen that a correlation already exists between C/S and RI.

## 6. Conclusions

From the Pilot Plant experiments, it has be proven that The ZEWA process is able :

1) Presently to treat economically by products from the main industries, with environmental advantages ($CO_2$, natural resources savings)and valuables final products ( iron alloys and slags)

2) In the future to contribute to general knowledge of the hydraulicity and useable properties of blast furnace slag by the production of a tailored slags in large quantity whereas it is difficult to modify the chemistry or the mineral composition of industrial BF slags.


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## References


[1]J. Borlee, A. Fleischander, U. Genarry, M. Gimenez, F. Sorrentino, J.M. Delbeck, C. Grivard, J. Hoffman, J. Calloens, K. Kubica,E. Roubaud, M. Raclavsky, Nouveau procédé métallurgique pour la production de phases métalliques et minérales valorisables à partir de coproduits générés par la sidérurgie et d'autres grands secteurs industriels. Revue de la métallurgie CIT (1) (2005) 60-67

[2]J. Borlee, A. Fleischander, U. Genarry, M. Gimenez, F. Sorrentino, J.M. Delbeck, C. Grivard, J. Hoffman, J. Calloens, K. Kubica,E. Roubaud, M. Raclavsky, ZEWA, a new metallurgical process for the production of valuable metallic and mineral materials from by products generated by the steel industry and other major activity. Scanjet conference (2005)

[3] W. Gebert, U. Gennari, Results from the ZEWA pilot plant in the Vitcovice steel plant, International conference on stainless steel plant product Prague (2004)

[4] H. Pirker, Method for conditioning slag with the addition of metallurgical residual additions and installation for the same, Patent W.O 00/75385, 03/07/1990

[5] A. Fleischander, U. Gennari, Zero waste steel works, valuable products from byproducts, presented at the 5th International symposium of on Waste processing and recycling in mineral and metallurgical industry. Canadian Institute of mining, metallurgy and petroleum ( 2004)

[6] F. Sorrentino, M. Gimenez, Composition minérale hydraulique et son procédé de fabrication, French Patent N° 0351118 18/12/2003

[7]J.N. Murphy,T.R. Meadowcroft, P.V. Barr,Enhancement of the cementitious properties of steelmaking slag,.Canadian metallurgical quaterly ,36, (5), (1997), 315-331

[8] M. Kühn, P. Drissen, J. Geissleir, H. Shrey, Improving if slag quality by injection treatment, Revue de metallurgie CIT, MTS, JSI (2001 )150-155

[9] V. Poupardin, F. Sorrentino, Method for oxidising treatment of steel plant slag to obtain cement based material, Patent W.O 02/062720A1, 15/08/2001

[10] F. Sorrentino, G. Chaperon, J.P. Bayoux, Method for oxidising treatment of steel work slags and resulting LD slag, Patent W.O 01/90019A1 29/11/2001

[11] G. Ye, E.Burstom E.,M. Kuhn , J. Piret, Reduction of steelmaking slags for recovery of valuable metals and oxides materials, Scandinavian journal of metallurgy 32, (2003) 7-14

[12] J.K Pargeter, J.A. Mc Dougall, G. Rottman,H. Vorverk, W. Reichel Ironmaking using the Inmetco process and related technologies, Proc $44^{th}$ Iron making Conf ISS-AIME (1985), 255-87

[13] F.W. Locher, Hydration properties and hydration of glasses in the system C-A-S, $4^{th}$ ICCC Washington (1960) 267-276




michel.gimenez@lafarge.com, francois.sorrentino@club-internet.fr

[14] G.A. Rankin, F.E. Wright, The ternary system CaO, $Al_2O_3$, $SiO_2$ Amer.J. Sci 39, (1915), 1-79
[15] P.Z. Wang, R. Trettin, V. Rudert, R. Umlauf,Influence of Al2O3 content on hydraulic reactivity of granulated blast furnce slag, and the interaction between Al2O3 and CaO, Advances in cement research, 16, (1), (2004) 1-7
[16] M. Gimenez, C. Bouillon, F. Ferey, F. Sorrentino, Properties of artificial slags produced by the ZEWA process, 27th International. Conference on cement microscopy.ICMA (2005)
[17] Slag Atlas, edited by Veh ( Verein Deutscher Eisenhüttenleute) (1995), p 10
[18] H.G. Smolczyk, The effect of chemistry of the slags on the strengths of slag cement, Zement Kalk Gips ( 6), (1978) 180-181
[19] E. Demoulian, P. Gourdin, F. Hawthorn, C. Vernet:, Influence of slags chemical composition and texture on their hydraulicity " 7 ICCC Paris 1980 ( III), (1980), 89-94
[20]C. Schneider , B. Meng, Bedeutung der glass structur von Hütten sanden fûr ihre reactivitât, 14 Internationale Baustofftagung (IBAUSIL) band 1, (2000) , 0455-0463
[21] P.Z. Wang, R. Trettin, V. Rudert, R. Umlauf, Recrystallisation of granulated blast furnace slags and the significance for the hydraulic reactivity, Advances in cement research 15, (1), (2003) 29-33


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