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Environmental aspects of the utilization of steel industry slags

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The utilization of blast furnace and BOF slags has long traditions and well-known applications in the building and road construction industries and in soil conditioning. The starting point for product development has been the basic physico-chemical properties of slags. This development has led to the almost 100% utilization of blast furnace slags and also considerable amounts of steel slags. While new methods and applications are continuously being looked for and developed in order to recycle and utilize all types of slag, there is at the same time an increasing debate over the exact nature of the slags, whether they are products or waste material, and whether they should be considered substances or preparations. These questions have emerged as a consequence of the environmental effects of the slags and current environmental legislation.

The environmental effects of slags can be seen to be both beneficial and less beneficial. There is no doubt about their benefits in the road construction industry, as they allow significant savings in terms of natural materials and in transportation. It is also a known fact that using slags as fertilizers and in the cement industry leads to reduction in CO_2 emissions. The less favourable effects are the possible harmful emissions into the soil and groundwater. In this paper we describe the properties of slag products and their environmental effects according to investigations carried out in Finland.

Keywords: utilization, blast furnace slag, steel slag, properties, solubility, environment

Introduction

Blast furnace and steel slags have been utilized worldwide for more than a century, mainly for road construction, in the building industry and for soil conditioning. The powerful emphasis on research into slag products and the development of applications for them has increased the utilization of the most popular slag products markedly. Production figures for the Raahe and Koverhar Steel Works in Finland are presented for the year 2002 in Table I, and the amounts of slag products used for various purposes are presented in Table II.

The main areas of utilization for blast furnace slags are in road construction and the cement industry, while steel slags are used in Finland almost solely for soil conditioning and for internal recycling within steelworks. Blast furnace slags are utilized up to 100 per cent and steel slags almost up to that level. Altogether 130 000 t of steel slags were used for soil conditioning in Finland in 2002, representing 15 per cent of the Finnish market. In addition to Rautaruukki's and Fundia's blast furnace and steel slags, AvestaPolarit's ferrochrome slag from its Tornio works is also used in both granulated and crushed form for road construction and in the construction materials industry. Altogether 350 000 t of ferrochrome slag are utilized annually.

With the world production of steel at about 900 million tonnes in 2002, the amount of by-products generated was over 300 million tonnes. Thus the environmental impact of these steel industry by-products is above all a matter of volume. In most countries blast furnace slags are utilized up to 100 per cent, the trend being towards increased granulation processing. The degree of utilization of steel slags extends to 75–85 percent. The use of steel slag for road construction and as a fertilizer and its recycling in the steelworks has generally decreased, while its use in the manufacturing of building materials has increased[1]. Thirty million tonnes of blast furnace slags were utilized in Europe in 2000, 56 per cent in the cement industry and 40 per cent in road construction. The utilization of all slag products in Europe in 2000 is presented in Figure 1[2].

The properties of slags

The basic chemical components of the metallurgical slags produced at the Raahe and Koverhar steelworks are presented in Table III. Nearly all of the Raahe blast furnace slag is watergranulated, while all of the Koverhar slag is aircooled. The properties of the slags vary according to changes in the process parameters, their chemistry being dictated by the desirable properties needed of the slag in the production of pig iron, and the physical properties are determined by the functioning of the granulation process as well as the blast furnace parameters[3]. The compositions of the blast furnace slags correspond to the mineral phases merwinite and melilite. The inadequate amount of cooling water used and the high temperatures of the water increase the porosity of the slag, thus increasing its water content, an undesirable property especially in connection with use in the cement industry. The Raahe blast furnace slag has a low Al_2O_3 content, which may have a negative effect on its reactivity when used as a binding agent. The higher alkalinity of the slag obtained during 2003 has nevertheless increased its reactivity to an extremely good value, as can be seen in Figure 2.

Table I
Production at the Raahe and Koverhar Steelworks in 2002

	Raahe Steelworks (1 000 tons)	Koverhar Steelworks (1 000 tons)
Hot metal	2 306	522
Crude steel	2 624	533
Blast furnace slag	481	91
Steel slag	177	54
Desulphurization slag	68	
Ladle slag	56	

Table II
Amounts of slag products used for various purposes in Finland in 2002

	Raahe Steelworks (1 000 tons)	Koverhar Steelworks (1 000 tons)
Road construction	382	69
Cement industry	116	29
Soil conditioning	111	53
Internal use in steelworks	51	38

The general trend in steel production has been for a lowering in the amount of slag per ton of hot metal produced to around 200 kg/ton, but due to the requirements of the process, the amount and composition of the slag will change, which will also affect the properties of the granulated slag. During April–May 2003 the amount of slag generated at the Raahe steel works grew to 250–260 kg/t pig-iron, which together with other changes in process parameters and malfunctioning of the granulation process enabled some slag to crystallize during granulation, lowering the degree of amorphousness.

The leachabilities of blast furnace slags have been determined on several occasions, employing a range of methods. According to NEN 7341 maximum solubility tests, neither granulated blast furnace slag nor air-cooled slag passes harmful components into the environment in significant amounts. Also, according to the NEN 7343 column test as performed on granulated and air-cooled blast furnace slags, all the limits proposed by the Ministry for the Environment for covered materials to be used in earth construction are much higher than the actual experimentally determined solubilities of the slags as presented in Table IV[4]. However, leaching of sulphate from air-cooled blast furnace slag is a known phenomenon, which should be considered when using slags in groundwater areas. The Dutch values are also presented in Table IV, since they are used in Finland as the basis for limitations on the use of materials in earth construction.

The main factor causing concern regarding utilization of the Koverhar blast furnace slag for road construction purposes is particularly the high sulphur content. All of the Koverhar slag is air cooled, which allows the structure to organize into crystalline phases of gehlenite, merwinite, monticellite, oldhamite, perovskite and spinel. Oldhamite tends to be quite easily soluble, thus liberating sulphate into the surroundings under favourable redox conditions. Attempts have been made to prevent the dissolving of sulphates from the Koverhar blast furnace slag by using steel slag in a mixture with blast furnace slag. According to the column tests, the addition of steel slag increases the pH of the leachate and markedly reduces the amount of sulphate liberated, Figure 3 and Table V. This property may lead to an increase in the utilization of steel slag together with Koverhar blast furnace slag in the road construction. In column experiments the pH of the leachate was adjusted to 4.0 with nitric acid in order to characterize the behaviour under Finnish rainwater conditions.

The growing interest and concern regarding slags used for soil conditioning is focused on their heavy metal concentrations. Due to the high temperatures of the processes, the concentrations of elements such as Cd and Zn are low, and the values obtained for the heavy metals present in all the slags are well below the limits dictated by the legislation applying to fertilizers (Table VI). For steel slags, however, the authorities still experience some concern regarding their chromium content. According to long-term experiments conducted in Germany with steel slag liming materials, steel slags do not increase the content of mobile chromium in soil to a significant extent, neither has any significant increase in chromium been observed in plants due to the use of steel slags[5]. This fact also highlights the importance of studying the real effect of a material under conditions as close as possible to the actual environment in which it is used.

MgO concentrations in the Raahe steel slag increased during 2002 due to the use of dolomite in the BOF process in order to minimize wear on the converter linings. The increased MgO is incorporated into the cubic structure of wustite (magnesiowustite) in the steel slags. Although MgO itself is regarded as a fertilizing component and has no harmful effect on the environment, there is usually a greater demand for CaO than for MgO in cultivated areas of Finland. Thus compositional changes of this kind can affect the marketing and the use of slags for soil conditioning. The use of dolomite has ceased since the testing.

Benefits of slag products vs. possible harmful effects

The benefits of using slags are well known and must be made quite obvious in order to exploit them for business

Table III
Basic chemical components of the Raahe and Koverhar slags

%	1	2	3	4	5	6	7
CaO	38.6	35.9	49.7	58.4	36.9	50.5	50.0
SiO_2	37.2	31.2	11.4	13.8	41.6	9.5	10.0
MgO	10.9	15.8	6.5	0.9	9.6	2.0	8.0
Al_2O_3	9.6	12.6	1.3	0.9	2.7	35.5	29.5
S	1.3	2.3	0.1	0.1	0.3	0.2	0.3
Ti	1.1	1.9	0.5	1.1	2.1	0.7	0.7
Mn	0.6	0.1	3.1	1	1.4	0.9	0.7
Fe_{tot}	0.5	0.2	18.5	14		0.9	0.7
P		0.004	0.3	0.2		0.01	0.01

1. Raahe blast furnace slag
2. Koverhar blast furnace slag
3. Raahe steel slag
4. Koverhar steel slag
5. Raahe desulphurization slag
6. Raahe ladle treatment slag 1
7. Raahe ladle treatment slag 2

Table IV
Leachabilities of slags (mg/kg) in NEN 7343 column tests.
The proposed concentration limit 1 is for uncovered structures and limit 2 for covered structures

Component	1	2	3	Proposed Finnish values for maximum concentrations		Proposed Dutch values for maximum concentrations	
				Limit 1	Limit 2	Limit 1	Limit 2
As	< 0.01		< 0.01	0.14	0.85	0.88	7.0
Ba	0.3–2.8		1.8–2.0	10	28	5.5	58
Cd	< 0.001		< 0.001	0.011	0.015	0.032	0.066
Co	< 0.01		< 0.01	1.1	2.5	0.42	2.5
Cr	< 0.01		0.01–0.1	2.0	5.1	1.3	12
Cu	< 0.10		< 0.01	1.1	2.0	0.72	3.5
Hg	< 0.001		< 0.001	0.014	0.032	0.018	0.076
Mo	< 0.05		< 0.05	0.31	0.50	0.28	0.91
Ni	<0.1		0.2	1.2	2.1	1.1	3.7
Pb	< 0.01		<0.01	1.0	1.8	1.9	8.7
Sb	< 0.01		< 0.01	0.12	0.40	0.045	0.43
Se	< 0.050		< 0.050	0.060	0.098	0.044	0.10
Sn	< 0.01		< 0.01	0.85	3.1	0.27	2.4
V	0.9–1.2		0.03-0.06	2.2	10	1.6	32
Zn	0.03–0.1		<0.1	1.5	2.7	3.8	15
Cl-	7–95		3–41	250	-	600	8800
SO_4^{2-}	<200	2550	< 200	1500	-	750	22000

1. Raahe blast furnace slag
2. Koverhar blast furnace slag
3. Raahe and Koverhar steel slag

purposes. Their use in earth and road construction enables savings of up to twice the amount of non-renewable natural material, due to the better bearing capacity and thermal insulation properties of slags. They can be used in road construction for massive structures, as an aggregate in bituminous pavements and as a binding agent in base courses, as well as for strengthening the subsoil[6].

The use of slags for soil conditioning and in the cement industry likewise saves natural resources, and in addition reduces CO_2 emissions. The calculated savings in the latter respect achieved in Finland in 2002 are presented in Table VII. CO_2 emissions are becoming an increasingly important factor in industry with the ratification of the Kyoto protocol.

In soil conditioning, laboratory and field experiments have proved that slags are almost as efficient in their neutralizing effects as carbonate limes[7]. In addition to a neutralizing effect, siliceous liming materials include macro- and micronutrients such as sulphur and magnesium. Blast furnace slag possesses a high phosphorus sorption capacity and the sorbed phosphorus is found to remain largely in a form in which it is available to the plants. The heavy metals in slags are quite low in concentration and tend to be tightly bound to the slag matrix, as shown by leaching tests[8]. In addition, siliceous liming materials improve the soil structure and reduce infection by fungal diseases. Thus all these factors point clearly to the benefits of using slags as liming materials, eventually leading to better yields, soil protection and savings in natural resources[9].

The possible harmful effects of slags are introduced mainly by certain components present in air-cooled blast furnace and steel slags. Proper use of these products usually prevents the harmful effects from causing any environmental problems, but research is continuously being done into the effects of certain heavy metal concentrations in steel slags in order to characterize their effects thoroughly.

Environmental regulations concerning the use of slags

Finland has been one of the leading countries in the discussion of the status of slags between the authorities and the steel industry. The environmental authorities tend to overlook the benefits of the utilization of slags in their search for harmful effects and their urge to classify slags as waste. On a European scale, the following regulations govern the use of slags[10]:

1. Directive on waste
2. List of wastes (EWC 2000)
3. The European Shipment of Waste Regulation and the Green List of Wastes
4. The IPPC Directive
5. BAT on the production of iron and steel

The definition in the Directive on waste is: 'waste' shall mean any substance or object which the holder discards or intends or is required to discard. According to the European Waste Catalogue, wastes from the iron and steel industry are 10 02 01 waste from the processing of slag and 10 02 02

Table V
Amounts of sulphate determined in leachates from the Koverhar blast furnace slag-steel slag mixtures in column tests

Column no.	Amount of steel slag	Measured pH	Sulphate [mg/L]	Volume
1	100%	12.2	30	0.96
2	100%	12.3	20	0.96
3	0%	10.7	150	1.05
4	0%	10.2	780	0.97
5	50%	12.0	10	1.00
6	50%	12.0	15	1.04
7	10%	12.1	40	0.99
8	10%	12.2	45	1.02
9	30%	12.2	20	0.97
10	30%	12.2	45	1.00

Table VI
Concentrations of heavy metals in soil conditioners and limit values (mg/kg) for Finland

	1	2	3	4	Limit values
Hg	0.05	0.05	0.04	0.12	2.0
Cd	0.10	0.10	0.10	0.10	3.0
As	4.60	6.00	1.00	1.02	50
Ni	5.67	2.80	7.00	12.83	100
Pb	1.00	1.00	1.00	1.00	150
Cu	7.50	5.80	16.50	22.17	600
Zn	2.50	1.60	4.00	5.26	1500

1. Raahe blast furnace slag
2. Koverhar blast furnace slag
3. Raahe steel slag
4. Koverhar steel slag

Table VII
Savings in CO_2 emission in Finland in 2002 achieved by the use of steel industry slags in the cement industry and for soil conditioning

	Amount of slag used	Savings in CO_2 emissions
Binding agents	104 200 t	83 400 t
Liming material	161 300 t	67 100 t
Total	265 500 t	150 500 t

unprocessed slag. The starting point for slag producers is that slags are never intended to be discarded, never leave the chain of utility, and should therefore not be regarded as waste. On the contrary, slag is an industrial co-product produced during the making of iron and steel, a product whose chemical and physical properties are tightly controlled according to specific parameters. This means, that there is a primary intent to make quality-controlled slag from which the holder can process slag products, which fulfil the requirements laid down in the appropriate standards. Thus the processing of slag would cause it to cease to be classified as waste[11].

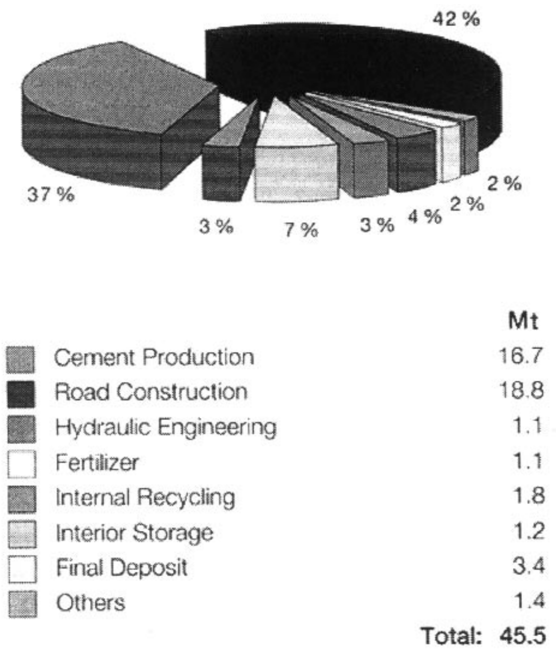

Figure 1. The use of slags in Europe 2000 (website of Euroslag).

If slags were classified as waste, this would have a dramatic influence on their utilization, making it time consuming and financially unattractive. The producers and the end-users would need to apply for permission to use the products and production costs would rise significantly. The application procedure for permission is a slow process, without any guarantee regarding the length of time required or the outcome. There is no need to mention the harmful effects on the image of the products and for the possible users.

Summary

The steelmaking industry places great emphasis on sustainable development and a general target is the concept of the waste-free steel mill. This implies an optimal extent of utilization of the co-products arising from steelmaking. Slags, which are an integral part of iron and steelmaking processes, comprising more than 80 per cent of all co-products, are of crucial significance when environmental matters are to be taken into account. The principal premise for the use of slags has been a thorough knowledge of the basic properties of different kinds of slag and product development grounded in a knowledge of these properties.

At the same time as the use of slag products has been growing, the environmental requirements have been tightened and new legislation has been passed to regulate the use of slags. The fundamental question is how to classify slags in the light of the environmental directives, as a product or as a form of waste. This will be a very important matter of principle when considering the use of slags in the future. The classification of slags as waste may detract from their commercial utilization, thus weakening the notion of sustainable steelmaking in this respect. The final solution will perhaps appear in the near future, and the steel industry is naturally hoping for a decision, which will support the fruitful utilization of these co-products, rather than one, which imposes artificial barriers and is against the goals determined by the environmental authorities themselves.

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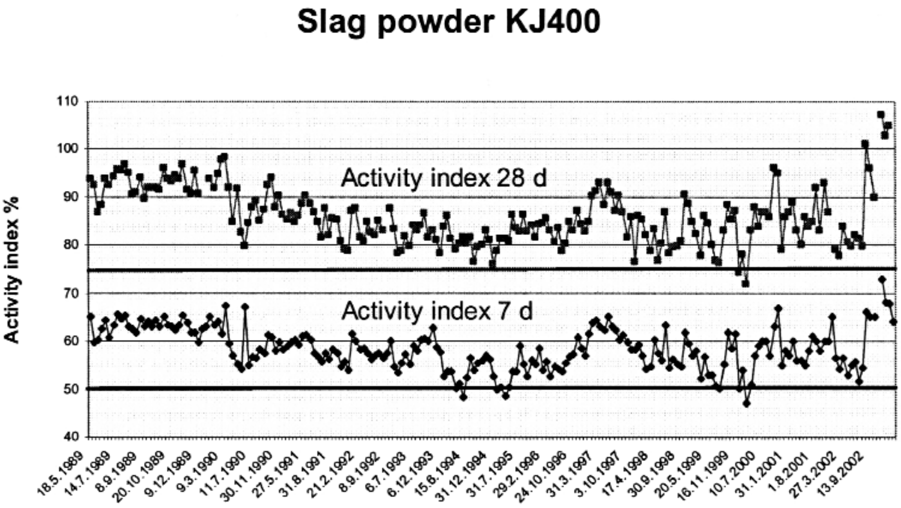

Figure 2. Reactivity of Raahe blast furnace slag powder KJ400

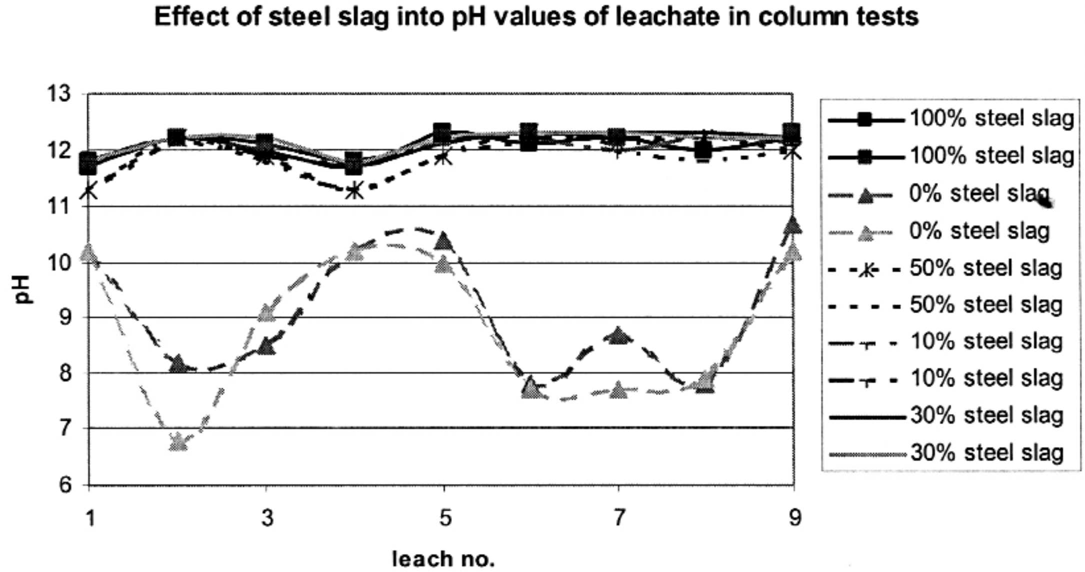

Figure 3. Effect of steel slag in mixtures of Koverhar blast furnace slag and steel slag on the pH of the leachate in column tests

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