



Sixth International Conference on

Molten Slags, Fluxes and Salts

Stockholm, Sweden - Helsinki, Finland 12 - 17 June, 2000

THE INFLUENCE OF CHEMICAL AND PHYSICAL PROPERTIES ON THE UTILIZATION OF SLAGS

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Slags are an integral part of iron and steelmaking processes and they have been commonly utilized on a broad scale ever since these processes were first taken into use. Besides the economic aspects, environmental requirements will enhance the need for further product development work concerning the properties of slags in the future, in order to observe the principle of sustainable development. The general target for the whole steel industry is the total utilization of all by-products.

This paper will discuss the current situation in integrated steelmaking in Finland and present some results of research into the main chemical and physical properties of slags with a view to their recycling and further utilization. In addition, comments will be made on the influence of post-treatment processes on the properties of slag products.

INFLUENCE OF CHEMICAL AND PHYSICAL PROPERTIES OF SLAGS ON THEIR UTILIZATION

Introduction

World production of steel has been approaching 800 million tonnes in recent years (Fig. 1), which has at the same time meant the generation of over 300 million tonnes of by-products, solid waste and sludge [1]. The quantities of these materials and their compositions indicate that environmental loading from the steel industry is above all a matter of volume. Steel as such is a fairly environmentally acceptable product, especially as far as its recycling potential is concerned.

The proportional distribution of the by-products and waste arising from steel production is such that more than 80% of the by-products are slags, the further processing of which into marketable products has been an object of increasing interest throughout the steel-producing world. The utilization of slags has developed up to now very largely in the form of either re-use within the steelmaking process itself or the creation of a wide range of recycled products.

The situation at the present moment is that blastfurnace slags are being re-used 100% in most countries and BOF steel slags to the extent of about 75 – 85%. The following trends have been observable in recent years:

- the granulation of blastfurnace slags has increased significantly
- the use of BOF steel slag in road building has decreased
- the use of steel slag for the manufacturing of building materials has increased
- the use of steel slag as a fertilizer has decreased
- the recycling of slags at the steelworks has decreased

The slags that arise in the steel industry are by-products from the main processes, the smelting of iron and steel, and their properties vary according to the optimization achieved in the manufacture of these main products. The possibilities for influencing these properties at the time when the slags are generated are therefore highly restricted, in spite of the fact that they are naturally of extreme importance as far as utilization is concerned. Consequently, means of adjusting or modifying the properties of slags through the use of additives, either immediately on their separation from the iron or steel or later, by re-smelting, have been an object of intensive research for some time. The question of how far the properties of the resulting slags can be taken into account when adjusting the parameters of the main processes without detracting from the quality of the products has not been considered in any depth, however.

The constant tightening of environmental regulations has had both favourable and unfavourable repercussions for the utilization of by-products. One favourable consequence has been that companies are obliged to reduce waste and aim at the highest possible degree of recycling. On the other hand, the more stringent environmental norms mean that the costs of developing commercial products from these materials become higher and threaten to restrict their use.

Utilization of slags from an integrated steel mill

The main species of slag to arise in an integrated steel mill are blastfurnace slag from iron smelting and BOF steel slag, which is produced in the oxygen converter in the steel process. These account between them for about 75% of all the by-products of the steel industry /1/. About twice the amount of blastfurnace slag is generated relative to steel slag. The slags arising from the pre-treatment of the molten iron prior to the steelmaking process, including desulphurization slag, and the molten crude steel ladle treatment slags, are of less significance in terms of reutilization.

Blastfurnace slag

The principal by-product of an integrated steel mill, blastfurnace slag, has been utilized on a regular basis for years, and although the slags from individual mills differ slightly depending on the raw materials used, they are fairly similar in composition. The products are traditionally used in the building materials industry, earthworks and road construction, and agriculture. The trend has been towards a reduction in the amount of slag generated per tonne of crude iron, as has been the case at the Raahe works of Rautaruukki Oyj, for instance (Fig. 2). A second significant trend has been an increase in the production of water-cooled slag at the expense of air-cooled slag.

The continuity of blastfurnace slag production and the good prospects for its utilization have led product developers to contemplate ever more demanding and diversified slag-based products (Fig. 3). Since the properties of the slags are to a great extent determined by their primary composition, this diversification and quality enhancement has involved modification, i.e. adjustment of the composition of the material by means of additives.

The effects of the composition of a slag on its viscosity in a molten state have been studied a great deal, and an extensive literature has emerged on the subject /2/. Of the main components, SiO_2 and Al_2O_3 increase viscosity while CaO and MgO reduce it, so that at constant temperature the viscosity is dependent on the ratio $(\text{CaO} + \text{MgO}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$. CaO can be at least partly replaced by MgO in a slag without any appreciable change in viscosity, but the effect of Al_2O_3 is more complicated, as it seems to increase the viscosity only up to a certain threshold concentration, after which any further addition will reduce it.

There are other components that also have a considerable effect on viscosity. The addition of alkaline metals to molten slag reduces it significantly, and MnO appears to have a similar effect, although inconsistent results have been obtained. Sulphur increases viscosity once its amount exceeds 2%.

The emissions of hydrogen sulphide associated with granulation can be avoided by adding only small amounts of sulphuric acid and iron sulphate to the granulation water. This will also reduce the sulphur content of the granules. A more common method, however, is to oxidize the sulphur to sulphur dioxide by blowing air, oxygen or steam into the melt in the slag channel or ladle. This causes the slag to become lighter in colour, denser and less porous.

Extensive laboratory tests were carried out in Finland during the 1980's on the modification of blastfurnace slags for various purposes /2/. Additions of phosphorus, potassium, copper and boron were made in the form of natural phosphorite, potash, technical copper sulphate and borax in order to achieve the optimum balance for a fertilizer. The required materials

were obtained by mixing the additives into granulated slag in the correct proportions, melting the mixtures in a furnace and cooling the resulting melts by the granulation technique. The properties of these materials were then subjected to solubility tests and used in growth experiments.

Attempts were made to produce mineral wool from slag by adding oxides that would increase its viscosity, notably SiO_2 and Al_2O_3 . Almost any material containing these oxides was regarded as a suitable source: grog, fly ash from a coal-fired power station, sand or a suitable mining gangue. The raw materials can in principle be handled in one of two ways. Either molten slag can be taken direct from the blastfurnace, in which case the mineral wool plant must be situated adjacent to it, or else air-cooled slag can be remelted in a cupola furnace, for instance, which allows greater freedom in locating the plant. The laboratory tests made use of molten slag, to which various chemicals were added to raise its melting point and viscosity, in order to obtain longer fibres with smaller numbers of spheres at their ends. The tests were supplemented with pilot plant experiments, which indicated that fibre formation improved more markedly the greater the modification made to the composition of the slag. Problems also emerged, however, as special measures are required to dissolve acid substances in molten slag.

Attempts were made to improve the binding properties of blastfurnace slag by raising the aluminium and calcium concentrations and determining the reactivities of the resulting materials. The point of departure for this was the observation that an increased slag Al_2O_3 content improves the strength of slag concrete up to a certain point. The aim of the research was to ascertain the effects of increasing the CaO and Al_2O_3 concentrations in Finnish blastfurnace slag from a hydraulic perspective. Tests were also carried out to assess the possibilities for producing specialized cements, i.e. sulphate cement and high-alumina cement. The various attempts at regulating the composition from the cold mixture onwards nevertheless failed to yield the expected results and the experiments never led to any factory-scale applications.

In addition to modification, laboratory experiments were also conducted to determine the effects of granulation conditions, notably temperature and cooling rate, on the hydraulic properties of the slag. The effects were shown to be negligible on a laboratory scale, however.

Attempts were made to reduce the relatively high volumetric weight of slag pellets, $2.0 - 2.2 \text{ kg/dm}^3$, by mixing various additives such as limestone, bauxite, gypsum, sand or calcium sulphide into the melt. The most effective of these were CaSO_4 , CaS and CaCO_3 , which lowered the volumetric weight by 9 – 14%.

All in all, the results achieved by this extensive programme of research failed to come up to expectations, nor did they lead to any new factory-scale applications, partly for economic reasons. The general conclusion must be drawn that although the modification of slags offers attractive prospects for the researcher, the practical applications of such techniques have proved to be relatively limited.

BOF steel slag

About 60% of the world's steel is produced nowadays in integrated steel mills by converting, a process that generates over 40 million tonnes of primary low-phosphorus (BOF) converter slag every year /1/. This material, which is the second most significant by-product of the steelmaking process after blastfurnace slag, is more variable in composition than the latter and has a high CaO content, its other main chemical components being SiO₂, MgO, FeO, MnO and Al₂O₃. The main components in terms of mineral composition are di- and tricalcium silicates, ferrites, wüstite and free calcium.

Although less work has been done to develop means of utilizing BOF steel slag than in the case of blastfurnace slag, the degree of utilization is around 75%. The possibilities for recycling primary BOF steel slag at the steel mill after removal of the metal content vary from one country to another depending on the chemical composition of the slag, steelmaking practices and national and local environmental regulations. Earlier it was common for about 30% to be recirculated via the sintering plant or smelter, but this practice has diminished or died out completely at many mills, usually because of more stringent environmental restrictions and increased loading of the processes with detrimental substances such as zinc, phosphorus or vanadium.

A certain amount of BOF steel slag is also used in the building materials industry, in marine construction, earthworks and road building and as a means of soil improvement, and the remainder is either stored or used for landfill purposes. The above-mentioned branches of the construction industry form by far the most important users of this material, accounting between them for 45 – 50% of the BOF slag produced.

One significant problem with the reuse of BOF steel slag is the high concentration of free CaO present in the more basic varieties both in residual, i.e. insoluble, form and in recrystallized form, in addition to which it may be formed secondarily as an alteration product of calcium silicate. The problem arises from the expansion of this free lime upon hydration, which can cause cracking in structures.

This expansion effect is well known worldwide, and a great deal of research has been put into solving the problem. Attempts have even been made to introduce norms for maximum permitted calcium content, and a limit of 4% CaO has been imposed on BOF steel slag for use in road construction work in some cases. It is not particularly easy to define reliably the concentration of free calcium in a slag, however, so that exact norms are not always justified. On the other hand, it has also been shown that the expansion of a BOF steel slag is not directly determined by its free lime content /3/, but is also dependent on its mineralogical composition and internal structure. This suggests that it would be more justified to attempt to determine the extent of expansion under standardized conditions and use this information to derive norms for the use of the material.

Attempts have traditionally been made to eliminate the expansion problem by allowing the slag to age out of doors for several months, and this has been found to work moderately well in practice. One condition for this, however, is that the slag should not be crushed again after ageing. Steam treatment has also been used on a factory scale with good results, but the problem with this is the high cost of the process /4/.

A method has been developed in Germany in which the free lime is removed by injecting oxygen (O_2) and sand (SiO_2) into the molten slag immediately after it is drawn off /5/. The resulting reaction leads to the formation of calcium silicate and calcium ferrite. This method has been implemented on a factory scale.

Secondary slags

In addition to the primary slags, various secondary slags are produced in the pre-treatment of the crude iron prior to converting and in the further processing of the steel after the converter stage. The most common form of pre-treatment is desulphurization, while desiliconization and dephosphorization are somewhat rarer practices.

Secondary slags are more difficult to recycle than primary ones, largely on account of their highly variable chemical and physical properties. Desulphurization slag has been recycled via the sintering plant and blastfurnace to some extent /6/, and there are some references to its utilization outside the mill, e.g. as a raw material for the manufacture of cement and as a soil improvement agent in agriculture if it has a high lime content /1/.

In summary, it may be said that the secondary slags are mostly used for various landfill purposes, and that their heterogeneous properties and the relatively small volumes generated have so far not inspired much research into possible modification techniques.

Utilization of integrated steel mill slags in Finland

The integrated steel mills at Raahе and Koverhar in Finland produced about 3 million tonnes of crude iron in 1999, about 3.1 million tonnes of molten steel and about 1 million tonnes of slag of various kinds (Table 1), of which blastfurnace slag made up 61%, primary BOF steel slag 26% and secondary slags 13%. Typical chemical compositions for the slags are listed in Table 2. It should be noted that the blastfurnace slags in particular, and to a great extent also the primary BOF steel slags, are fairly consistent in their composition, whereas considerable variations can occur in the composition of the desulphurization slag and even more so in the ladle treatment slag.

Blastfurnace slag

As is the case worldwide, the blastfurnace slags generated in Finland are used virtually entirely for road construction, in the building materials industry and for soil conditioning purposes. Following the installation of direct granulation facilities at the Raahе Steel Mill in 1995 and 1996, practically all the blastfurnace slag coming from there has been water-cooled, whereas that obtained from the Koverhar Steel Mill is air-cooled. Data on the utilization of blastfurnace slag in Finland in 1998 are presented in Fig. 4.

The blastfurnace slag obtained from the principal producer in Finland, the Raahе Steel Mill, is relatively acid, poor in Al_2O_3 (Table 2) and fine-grained, over 90% of it being of grain size under 2 mm. Its degree of vitrification is high, over 90%. Some criticism of its basic

properties has been voiced from time to time by customers in its main areas of utilization, i.e. earthworks, road construction and the production of binding agents. The crucial property in the last-mentioned case is the activity of the slag, which is dependent on many factors, of which the most significant are alkalinity, which should be relatively high, Al_2O_3 content and vitrification. Activity levels of granulated slag from Raahe and Koverhar in Finland and Cherepovets in Russia are compared in Table 3, which also evaluates the compression strengths of samples of concrete produced using these with figures for a reference sample. The results indicate that the Raahe and Cherepovets slags, which are similar in composition (Table 4), both have relatively low activity levels, whereas the slag from Koverhar, which is richer in Al_2O_3 and MgO , has an excellent activity level. Research is now in progress into the effects of an addition of Al_2O_3 on the blastfurnace process in Raahe.

Some problems have also arisen on account of the fairly high moisture content of granulated blastfurnace slag (Fig.5) and its occasional poor grindability, which is reflected in reductions in grinder capacity (Fig. 6). The high moisture content is connected with the porosity of the granules, which is in turn attributable to the viscosity of the slag and the granulation conditions. These grindability problems are connected with vitrification and grain size, which are similarly dependent on the above factors. One surprising observation to arise from recent research is that, contrary to expectations, ageing of the granulated slag does not seem to have any effect on its grindability or reactivity after the first two weeks.

On account of its fine grain size, directly granulated blastfurnace slag does not have the same bearing capacity during road construction work as coarse-grained granules, but this difference is eliminated later by virtue of the binding reactions that take place. Similarly, the “sticks”, or thin, sharp needles created in the granulated slag from time to time in the course of its treatment, can also make the material more difficult to handle. The number of such “sticks” is evidently linked to temperature and alkalinity, i.e. it is once more a matter of viscosity (Fig. 7).

The Raahe blastfurnace slag approaches the boundary between the melilite and merwinite fascies in composition, which may explain the variability in its properties. It is particularly important as far as its physical properties are concerned that it should not lie in the area where small fluctuations in composition have a pronounced effect on its melting temperature or viscosity. If this can be avoided, small changes in the analyses of the input materials will not be reflected in the evenness of functioning of the furnace or of desulphurization, or on the mobility of the slag.

The decisive properties as far as utilization is concerned are determined in the blastfurnace process itself, and only limited opportunities exist for influencing these later, e.g. during the granulation process.

BOF slag

The total amount of primary and secondary slags arising as by-products of steel manufacture in Finland in 1988 was 315 000 tonnes, of which 60% was BOF slag (Fig.8). The utilization of slags in the same year is shown in Fig. 9. The main use for BOF slag is as a soil conditioning agent in agriculture, which accounts for almost half of the BOF steel slag generated. Some is used in road construction, but about a third has to be stockpiled.

A considerable proportion of the BOF steel slag was previously recycled via the sintering plant at the Raahe Steel Works, but this was stopped in 1992 in order to reduce phosphorus loading. The decision was based on experiences from an experimental period in 1986 during which the BOF slag was omitted from the sintering process for a certain length of time, leading to a reduction in phosphorus from around 0.04% to 0.02% (Fig.10) in the sinter and from around 0.06% to 0.04% in the crude iron (Fig.11). Experiments suggest that the phosphorus level in steel could be reduced to 0.003 – 0.004%, so that P(max) in the steel leaving the mill would be 0.015%.

The discontinuation of this recycling outlet naturally made the whole question of utilization of this type of slag more complicated, and since then significant proportions of the slag have had to be stockpiled. Intensive research is now beginning to give reason to expect that increasing use can be made of this material in earthworks and road construction, but this will be dependent on finding a solution to the stability problems that have arisen.

The Raahe LD steel slag consists of di- and tricalcium silicates, dicalcium ferrites, wüstite and free lime, which is present in porous residual particles, as an alteration product of tricalcium and in crystalline form. It is possible for a slag to contain as much as 14% free lime even after a year of ageing. The best outcome from the reuse point of view would undoubtedly be an extremely fine-grained slag composed of dicalcium silicate, dicalcium ferrite and wüstite but with no porous residual lime or tricalcium silicate, but manipulation of the slag in the course of the steel production process may not prove to be very practicable.

Similarly factors connected with the treatment of the slag, such as the timing or extent of the hydration of the molten slag after pouring, do not seem to be capable of affecting the product to any great extent, with the exception of ageing. It must thus be admitted that there is still a great deal to do when it comes to research into the economic utilization of BOF steel slags.

Secondary slags

Utilization of the desulphurization and ladle treatment slags arising at the Raahe Steel Works has so far been restricted mainly to landfill use at the site itself. With a view to further exploitation, work has been carried out to determine its chemical, mineralogical and physical properties, and road construction tests have been performed, together with long-term assessments of its behaviour in such structures. Although the research is still in progress, it must be said that that it would not be realistic to expect any very demanding applications to arise from it. Apart from the composition of these materials, their physical properties also vary too widely to allow any advanced use to be made of them.

Summary

The chances of being able to utilize the slags generated by the steel industry in an economic manner are dependent in the first instance on their chemical and physical properties, which are in turn determined by the conditions under which the main processes, the manufacture of iron and steel, take place. Little attention would appear to have been paid to the properties of the slags arising as by-products when considering the optimization of these processes, in spite of their demanding nature as recycled materials, although it must be said that blastfurnace

slag in particular is generally quite well suited for future use when the main manufacturing process is optimized to the maximum extent.

Since the steelmaking industry, like many others, places great emphasis on sustainable development, it is important as far as the associated concept of the waste-free steel mill is concerned that the by-products should also be utilized to an optimal extent. Although metallurgists have not traditionally had to worry very much about the nature of the by-products generated with a view to their utilization, this must be looked on in the future more as a matter of common concern which can benefit from closer cooperation between the producers and users of such materials.

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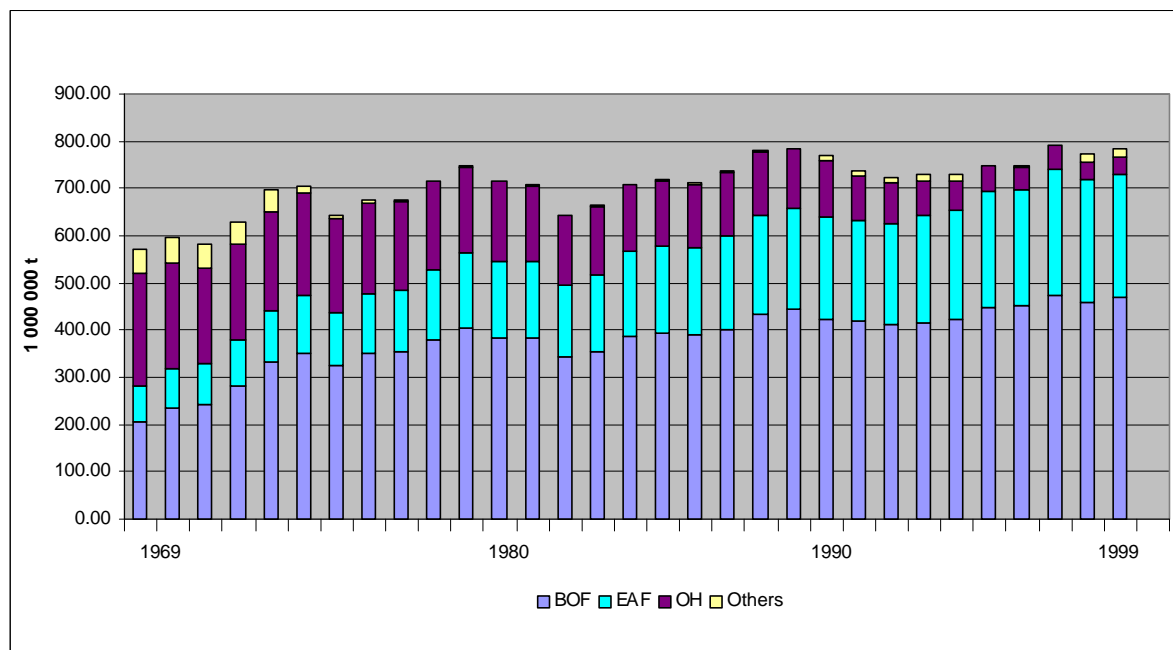


Figure 1. Crude steel production by processes 1969 - 1999, IISI Statistics 1999

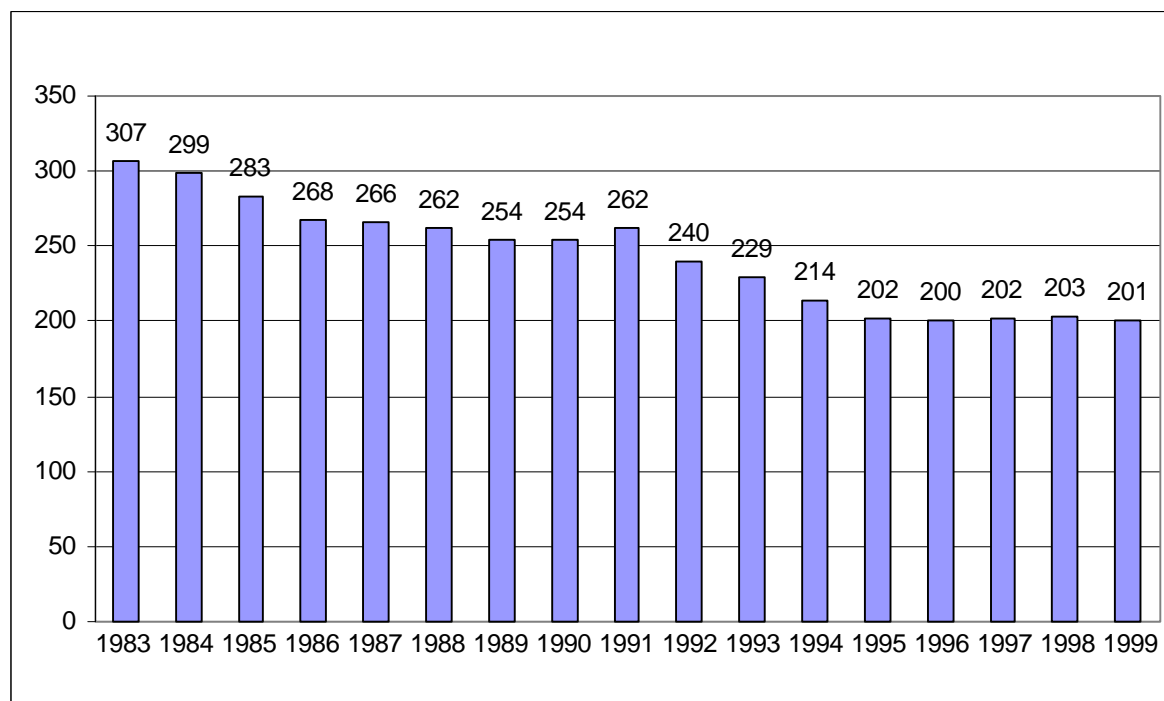


Figure 2. Slag Produced by the Raahe Steel Works Blast Furnaces 1983 - 1999 kg/t Hot Metal

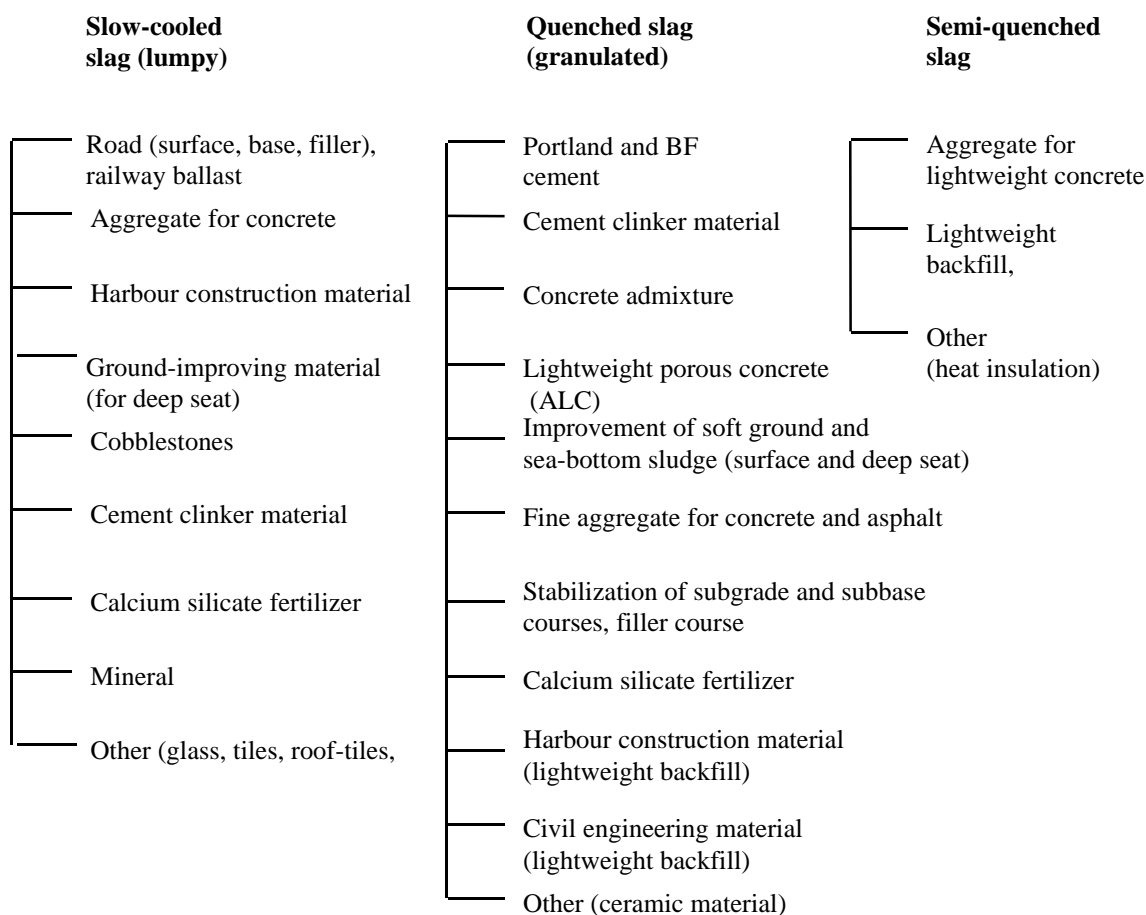


Figure 3. The Principal Uses of Blast-Furnace Slag

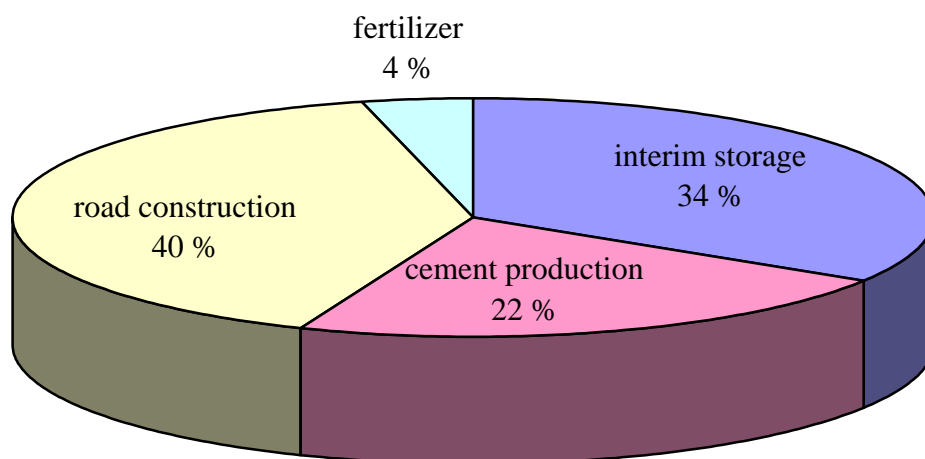


Figure 4. Utilization of Blast Furnace Slags in Finland in 1998.

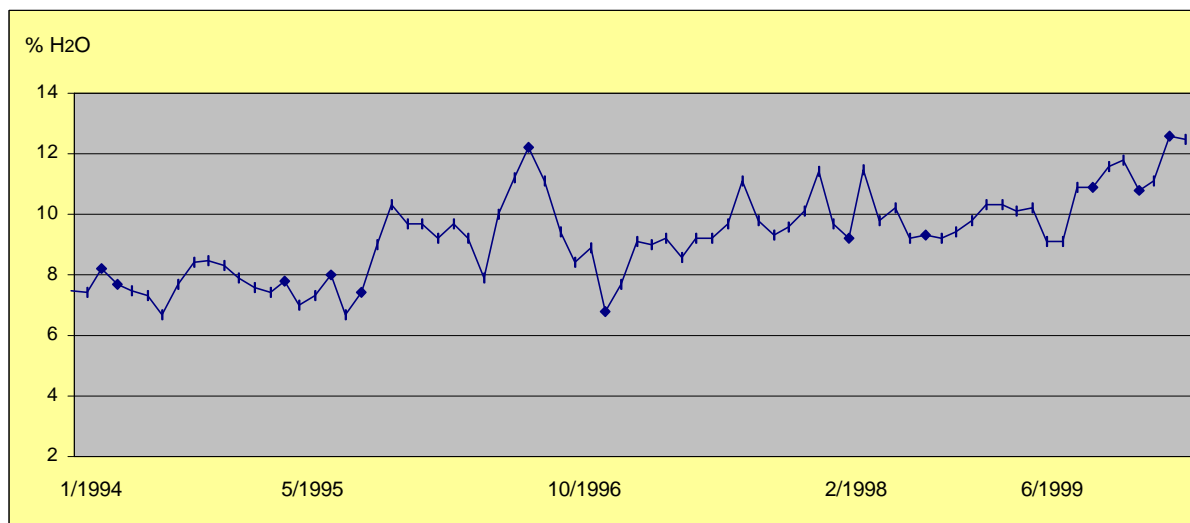


Figure 5. Moisture Variation in Granulated Blast Furnace Slag, Raahé 1994 - 1999

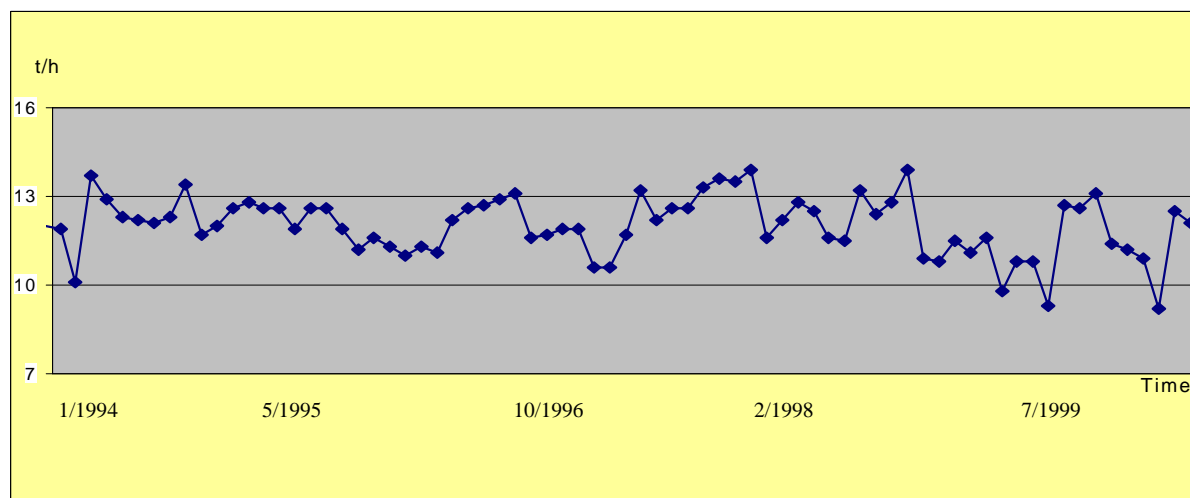


Figure 6. Mill Capacity for the Grinding of Granulated Blast Furnace Slag, Raahé 1994 - 1999.

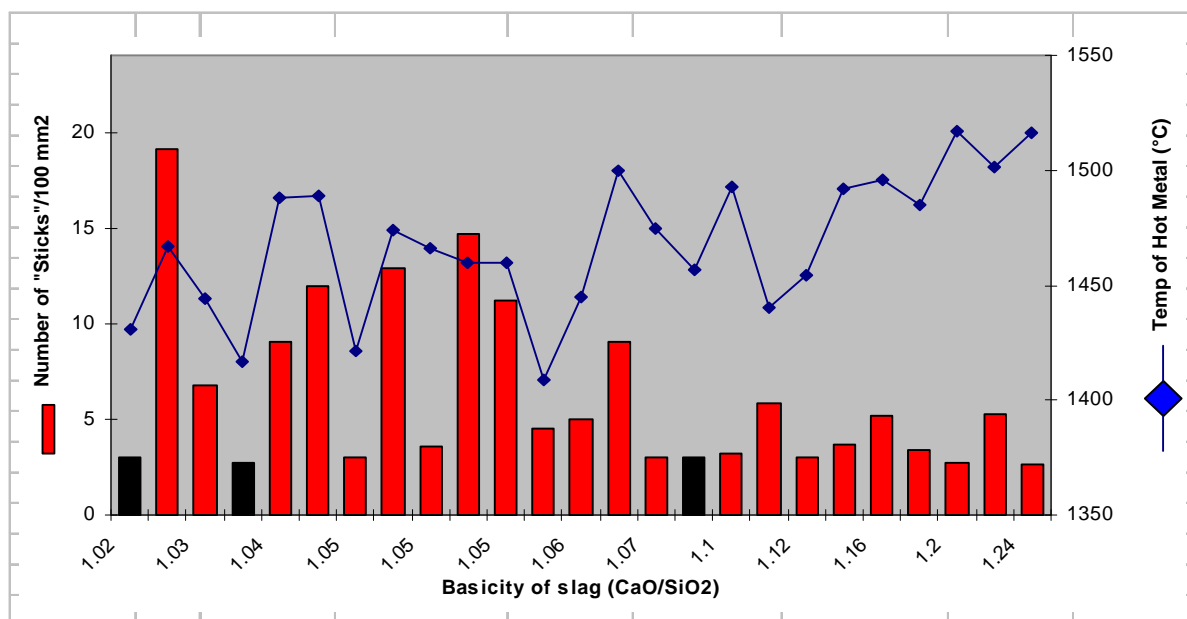


Figure 7. Influence of Basicity and Temperature on the Amount of "Sticks" in Granulated BFS.

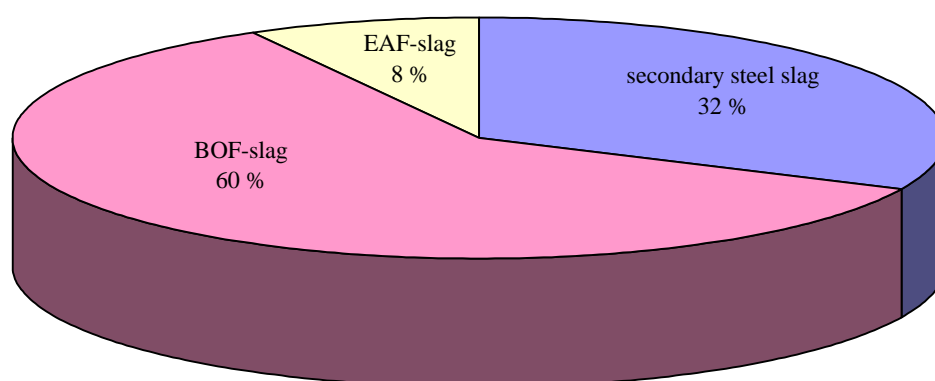


Figure 8. Production of Steel slags in Finland in 1998.

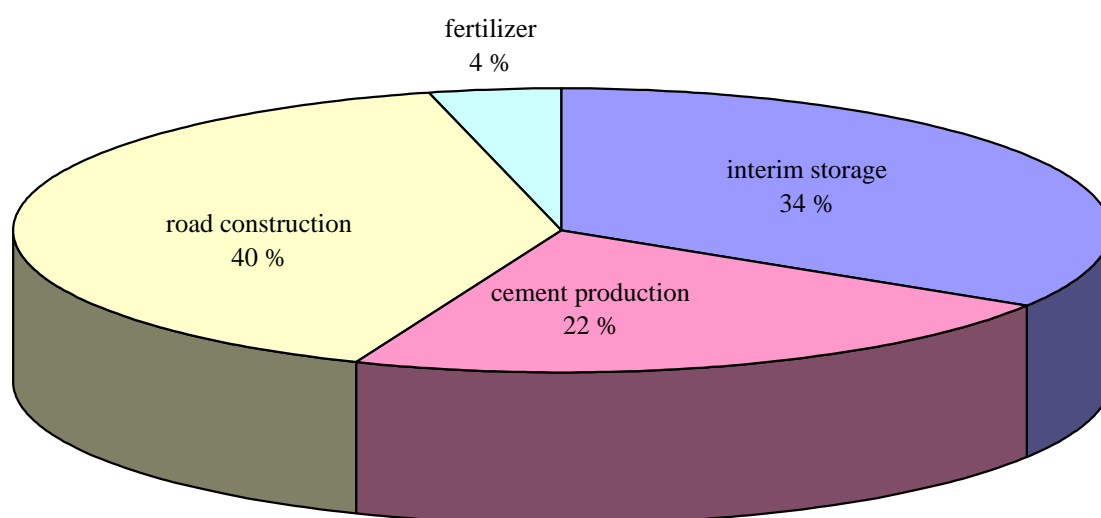


Figure 9. Utilization of Steels lags in Finland in 1998.

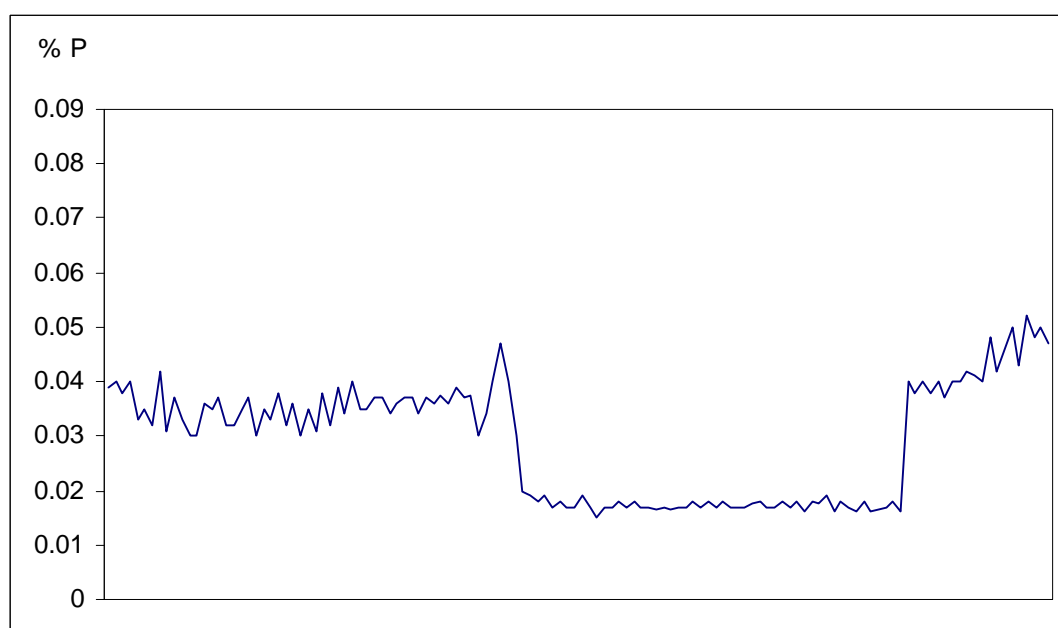


Figure 10. Reduction in Phosphorus in Iron Sintering at the Raahe Steel Works during the Experimental Period 30.11. - 28.12.1986.

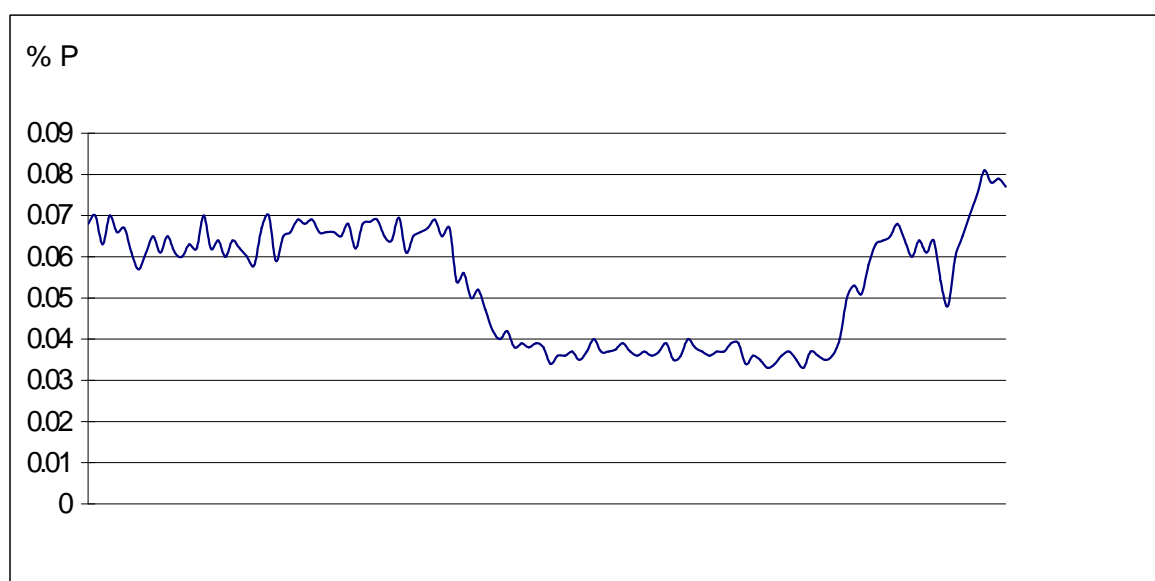


Table 1. Production at the Raahe and Koverhar Steel Works in 1999.

	Raahe Steel Works x 1000 t	Koverhar Works x 1000 t
Hot metal	2417	537
Crude steel	2572	547
BF slag	486	95
BOF slag	180	64
Desulphur. slag	80	
Ladle treat. slag	41	

Table 2. Analyses of Raahe and Koverhar slags

%	1	2	3	4	5	6
CaO	38,9	33,6	46,7	47,1	37,9	45,8
MgO	10,3	15,6	1,4	1,8	2,9	4,0
SiO₂	35,5	32,1	14,0	16,6	30,8	10,7
Al₂O₃	8,5	11,6	1,9	2,6	5,4	28,9
K₂O	0,7	0,5	0,1	0,1	0,8	0,1
Mn	0,5	0,1	2,4	0,8	0,7	2,0
Ti	1,3	1,1	0,9	0,9	0,6	0,5
S	1,5	1,8	0,1	0,5	2,1	0,2
Fe_{tot}	0,7	0,6	15,0	11,4	5,3	3,0
P	0,0	0,0	0,4	0,1	0,1	0,1

- 1. BF slag, Raahe**
- 2. BF slag, Koverhar**
- 3. BOF slag, Raahe**
- 4. BOF slag, Koverhar**
- 5. Desulphurisation slag**
- 6. Ladle treatment slag**

Table 3. Activities of Granulated Blast Furnace Slags (GBFS) from Raahe, Koverhar and Cherepovets

Specimen	Compressive strength MN/m ²		Activity index %	
	7d	28d	7d	28d
Cement CEM II A 42,5 R	46,6	54,4		
GBFS Cherepovets	28,4	45,4	61	84
GBFS Raahe	26,0	46,0	56	85
GBFS Koverhar	34,6	52,8	74	97

Table 4. Main Components of the Raahe, Koverhar and Cherepovets Granulated Blast Furnace Slags.

	Raahe	Koverhar	Cherepovets
CaO	38,9	33,6	40,3
MgO	10,3	15,6	8,1
SiO₂	35,5	32,1	39,0
Al₂O₃	8,5	11,6	8,0
K₂O	0,7	0,5	0,5
S_{tot}	1,5	1,8	0,8