PRODUCTION, CHARACTERISTICS AND USE OF FERROCHROMIUM SLAGS

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ABSTRACT

World HCFeCr production is 6.0 million tonnes. Correspondingly 1.1-1.6 t slag / t FeCr is produced depending on the raw material basis. Essentially all FeCr is produced in submerged arc furnaces, while the role of competitive technologies like DC is limited. In all furnaces fluxes are used to optimize the slag composition. Vital characteristics are smelting point, electric conductivity and viscosity. The main components of FeCr slag are SiO_2, Al_2O_3 and MgO. Additionally it consists of Cr-, Fe-oxides and CaO.

Granulated slag and/or classified slag products are produced depending on the production process. The slag products are mainly marketed in road and civil construction purposes but also in producing refractories. Normally crushed and screened slags are produced simultaneously when recovering alloy. The leachate of slag products is low and performance results are excellent. Slag products successfully replace natural sand and macadam. Generation of waste is essentially reduced. Producing and using slag products are described as BAT-technology and it is an essential environmental aspect.

Outokumpu Tornio Works produces 320 000 t FeCr-slag/a. This paper deals with formation of slag in smelting process, its chemical composition, physical and structural characteristics, utilization and product specifications as well as environmental aspects. The slag products are standardized and CE marked. Additionally the role of slag in smelting and alloy recovery is reviewed in this paper.

1. INTRODUCTION

World high carbon ferrochrome production, charge chrome and HCFeCr, was 6.0 million tonnes in 2005. The production increased by 2.8 per cent from the year 2004. Almost all ferrochrome is produced in submerged electric arc furnaces.

The raw material in the production of ferrochrome is chromite, which is chrome and iron oxides containing mineral. Chromite is used as lumpy ores or fine concentrates, which must be generally agglomerated to make them useable charge for the furnace. Fines in the smelting furnace cause unbalanced operation and thus decrease productivity. Different types of carbon are used to reduce metal oxides in the furnace. The most important of them is metallurgical coke. A careful quality control of raw materials ensures maximum output and uniform quality in the smelting process. Quartzite, bauxite, dolomite, corundum, lime and olivine are used as fluxing materials to get the right composition of slag.

The smelted products obtained from the smelting furnaces are ferrochrome alloy and slag. The slag production is 1.1-1.6 t / t FeCr depending on feed materials. Using modern process control and good quality charge materials the optimal slag composition can be attained. Important factors are temperature and composition of the slag, viscosity and electrical conductivity. The main components of the slag are SiO_2, MgO and Al_2O_3. The slag also includes Cr- and Fe- oxides and calcium oxide. Common phases in the slag are glass, spinels and forsterite. The slag chemistry is vital for the efficient ferrochrome production.

2. PRODUCTION OF FERROCHROME SLAG PRODUCTS

The raw materials used in the ferrochrome production are upgraded lumpy ore and fine concentrate from the Kemi mine. Fine concentrate is first ground and made into pellets in the sintering plant. The pellets are then sintered in the sintering furnace at a temperature of 1400°C. The charge of the smelting furnaces consists of pellets, upgraded lumpy ore, reducing metallurgical coke and fluxing quartzite. Before smelting the material is preheated up to 500–800°C by

burning carbon monoxide gas in a shaft preheater. There are two production lines in Tornio ferrochrome works, whose production capacity is 280 000 t FeCr/a. The smaller furnace transformer capacity is 40 MVA and that of the bigger one 75 MVA.

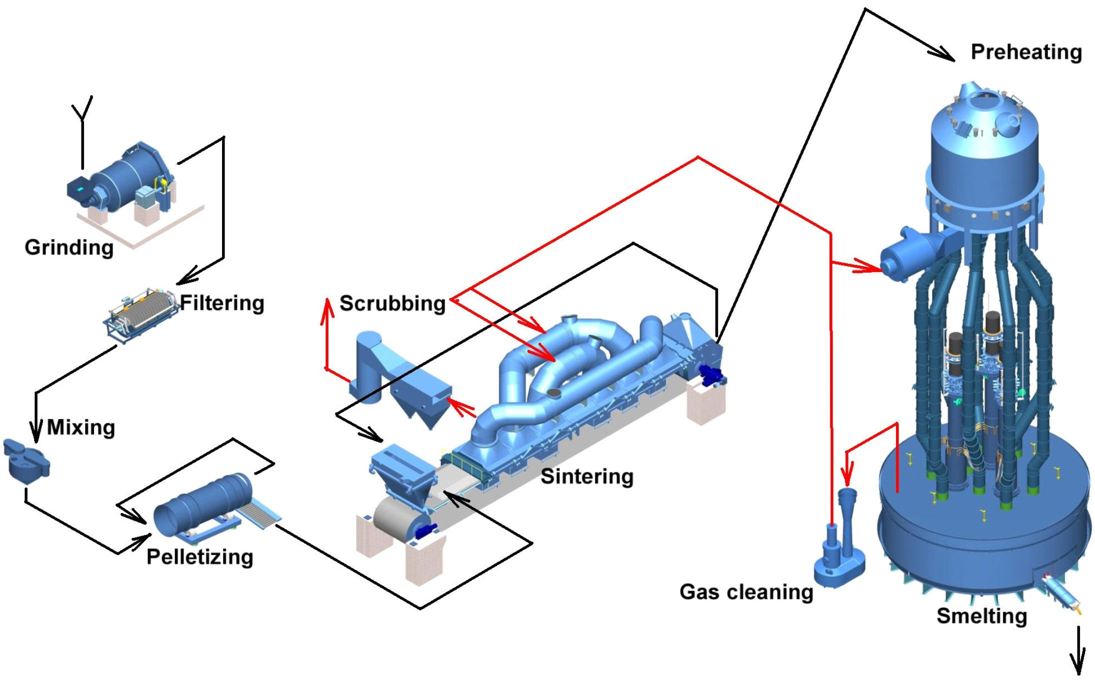

Figure 1: Outokumpu FeCr process

Chrome and iron oxides are reduced into metal in the submerged electrical arc furnaces by using metallurgical coke. Simultaneously part of silica is also reduced. Produced metal is classified as "charge chrome" quality, which includes 53 % Cr, 7 % C and 4-5 % Si. Typical reduction reactions in the ferrochrome furnace can be seen in Figure 2.

The other products in the smelting process are CO-gas and FeCr-slag. CO-gas results from the reduction reactions. It is generated at 700 Nm^3/t FeCr and it includes 85-90 % CO and 5 % H_2. In high temperatures the charge materials start to smelt. Materials not dissolving into metallic ferrochrome phases form primarily silicate phases, which are generated to form ferrochrome slag. The products obtained from the smelting furnaces, ferrochrome alloy and slag, are tapped into ladles at 2.5 hour intervals. The ferrochrome slag production is 1.2 t / t FeCr. It is mainly granulated and the rest is air-cooled. There is an in-house special handling and metal recovery process for the air-cooled slag, where it is made into finished products. In addition to recovered ferrochrome, classified slag products are also made. This process is operated by the subcontractor. Marketing of the slag products is also outsourced.

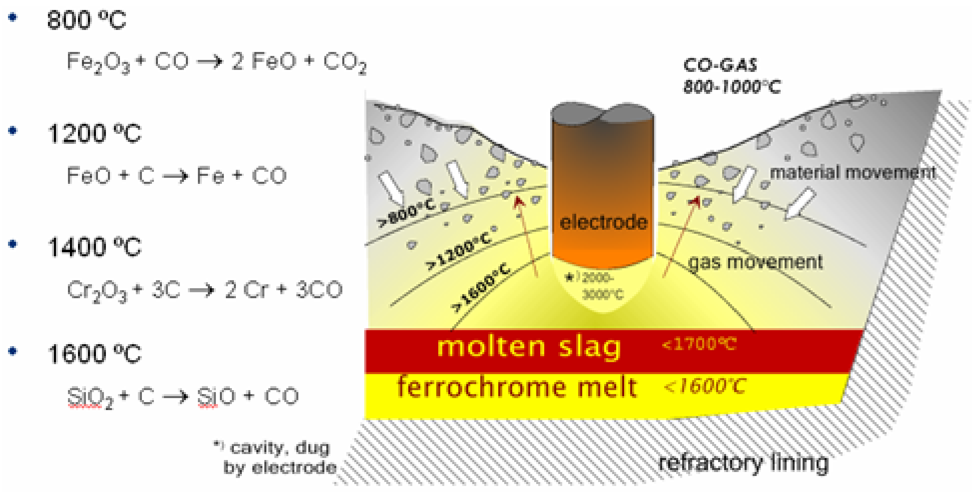

Figure 2: Typical reduction reactions in the ferrochrome furnace

2.1 Ferrochrome slag

The temperature of the slag in tapping is 1700 °C and that of the ferrochrome 1600 °C. The smelting point of the slag has to be higher than the metal smelting point, because metal is heated up by using slag liquid phase. The optimum smelting point has been practically noted between 1680-1720 °C. The composition of ferrochrome slag in the phase diagram is shown in Figure 3. The proportion of quartzite in the charge mix controls the right slag composition. The slag composition is tested every day by sampling and analysis.

The typical ferrochrome slag composition is 30 % SiO_2, 26 % Al_2O_3, 23 % MgO and 2 % CaO. The chrome content in the slag is about 8 % and the iron content 4 % respectively. Ferrochrome slag is acid. Its basicity is 0.8 when it is calculated by Formula 1:

$$B_3 = \frac{0{,}0178 \cdot \%CaO + 0{,}0248 \cdot \%MgO}{0{,}0166 \cdot \%SiO_2 + 0{,}0098 \cdot \%Al_2O_3} \tag{1}$$

The densities of metal and liquid slag are significantly different, so the slag will be separated from the metal. The density of the ferrochrome slag is between 2.5- 2.8 g/cm^3 and that of ferrochrome 6.8 g/cm^3. The viscosity of slag is a function of the pressure and temperature. The viscosity also has an essential meaning in the separation of slag and metal. The viscosity of the ferrochrome slag will increase when the content of SiO_2 and Al_2O_3 rise in which case aluminum-silicon chains also grow. An example of base slag values close to the ferrochrome process slag as a function of temperature is presented in Figure 4.

The total chemical composition of the slag defines the order of crystallization during the cooling process. The cooling rate has influence on the crystallization degree. It is crucially important for the smelting furnace operation that the charge materials and the products have optimum resistance values. The process slag of Outokumpu Tornio Works has a conductivity of 50 - 70 S/m calculated by the Johnston formula.

2.2 Ferrochrome slag products

The ferrochrome slag products are granulated slag as well as classified slag products made by crushing and screening. The main part of slag is granulated. The crushed and screened slag products are produced from air cooled lumpy slag which is collected from various process phases, e.g. from ladles and launders.

The slag is directly granulated during tapping where ferrochrome is tapped into ladles. The overflow from the ladles flows along the slag launder to the granulation pond, where high-pressure water breaks slag into

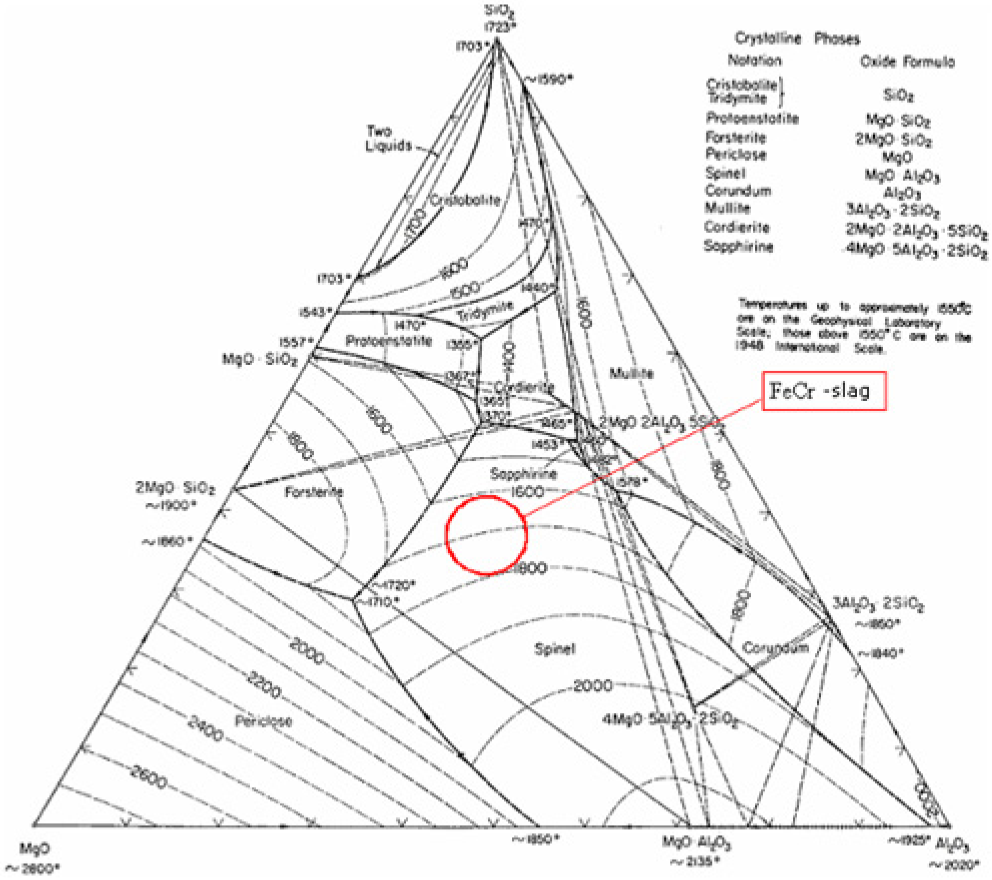

Figure 3: Phase diagram MgO-Al2O3-SiO2 [1]

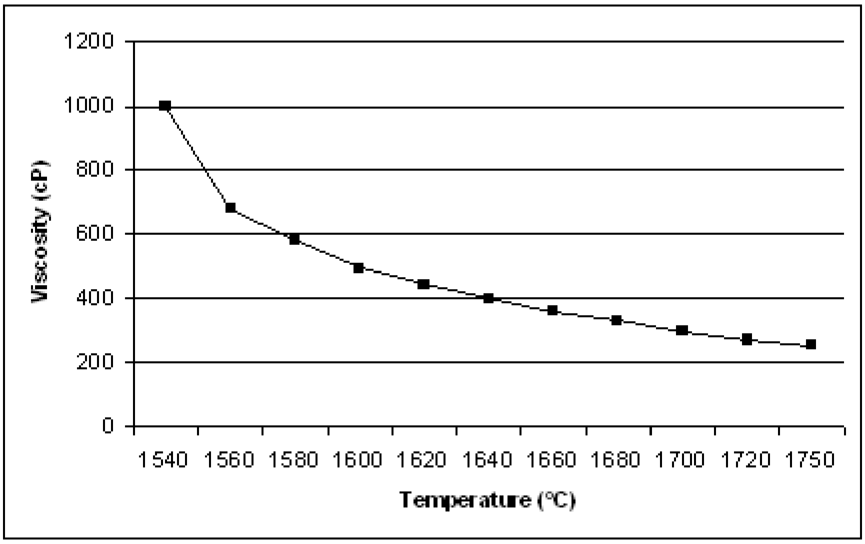

Figure 4: Viscosity of the base slag including 40 % SiO_2, 30 % Al_2O_3, 28 % MgO and 2 % CaO [2]

small fractions and efficiently it cools down. Granulated slag is a very homogenous product. The grain size is <6 mm. A granule is tight and partly crystalline. Typically the granulated slag includes three different phases, which are amorphous glass phase, crystalline and zonal Fe-Mg-Cr-Al -spinels and metal drops. The granulation process is shown in Figure 5.

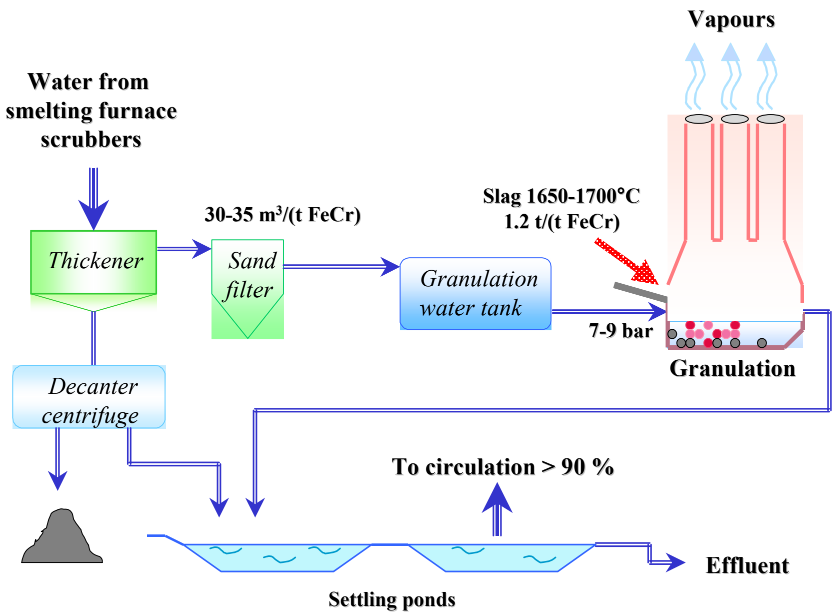

Figure 5: Slag granulation process

The ferroalloy separation from the lumpy slag happens in a special process, which is based on a gravity and magnetic separation. The first stage of slag processing is crushing and screening the feed material to fractions of 0-4 and 4-22 mm. Coarser fractions are handled by a heavy media separation - the DWP-method. A magnet separator and spiral washing are used for fine-grained material.

The recovered alloy of 0-4 and 4-22 mm are saleable products. The slag products from the process are aggregates of 0-4, 4-11 and 11-22 mm. The crystallization portion of lumpy slag is higher due to slower air-cooling than that of granulated slag. The structure of the slag is partly crystalline and partly glassy. Significant phases are amorphous glass, Fe-Mg-Cr-Al-spinels, forsterite, Mg-Al-silicate and metal alloy. The concentrating process is shown in Figure 6.

Particle size distributions of the granules and the gravels are controlled by weekly sampling and analysis. Compositions of all the products are analyzed more completely every two months from the weekly compilation samples. Measurements of the particle shape and durability against studded tyres are done on a monthly basis. An affinity to bituminous binders, a resistance to fragmentation and a durability against freeze/thaw are tested annually from the compilation samples.

2.3 Use of ferrochrome slag products

The ferrochrome slag products are chemically very stable. They are used in civil engineering and road construction and also, to some extent, producing refractory materials. Granulated slag is also used as subsurface drainage material. The ferrochrome slag products are quality assured and CE marked according to the standards EN 13242 and EN 13043 [3,4]. The main requirements for CE marking are the aggregate size and size distribution, resistance to fragmentation, durability against studded tyres and durability against freeze/thaw.

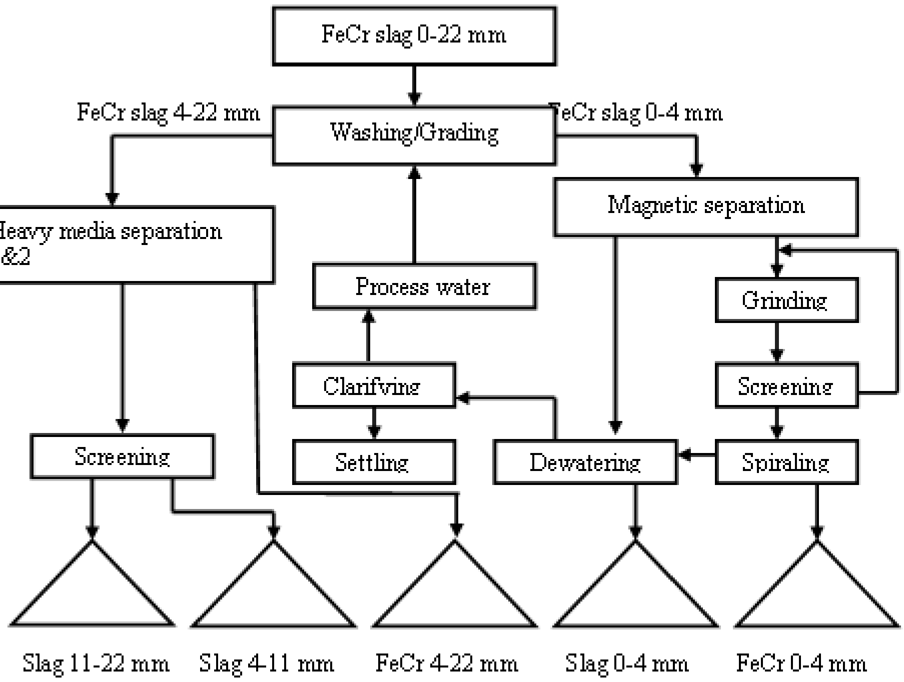

Figure 6: Slag processing for metal reclamation

Requirements for CE marking are coming gradually into general use in Finland from 2006. The ferrochrome slag products correspond with the standard SFS 5904 and they fulfill requirements of the standard EN 13285 [5].

They have their own CAS/EINECS numbers and operational safety bulletins.

The property requirements are checked every week by sampling and analyzing. The important properties of the slag products compared with natural material granite for civil engineering and road construction use is shown in Table 1.

Table 1: Properties of materials used in civil engineering and road construction

Character	*Granules*	*Gravels*	*Granite (crushed stone)*
Apparent density, Mg/m^3	1.10 - 1.35	1.40-1.70	1.5
Apparent density of structure, Mg/m^3	1.65 - 1.80		2.2
E- modul, static, MN/m^2	100 - 150		280 - 350
Thermal conductivity, W/mK	0.5 - 0.7	1.15	n. 2.0
Hydraulic conductivity, m/s	10^{-3} - 10^{-4}	$10^{-0.5}$ - 10^{-4}	-
Capillarity, m	0.10 -0.20	0.10 - 0.25	
Los Angeles value, %	-	18	

The ferrochrome slag products are excellent materials for road construction, because the removal of the earth is less and the need of new material for road is 30-50 % smaller compared with natural sand and macadam for example. Water easily penetrates slag layers. A hardness category of natural rock defines slag durability and hardness. The durability test result against studded tyres is A_N7. In that category the crushed and screened slag products fit in the best class I. The durability against freeze/thaw is good, F_1. The class of the resistance to fragmentation is LA_{20}. The particle size distributions are stabile. The typical distributions can be seen in Table 2.

Table 2: Typical particle size distributions of the ferrochrome slag products.

Product	*Particle size, mm*								
	-22.4	-16.0	-11.2	-8.0	-5.6	-4.0	-2.0	-1.0	-0.063
Granules					93	89	69	30	0.4
Gravel 0/4					99	88	62	44	0.4
Gravel 4/11			100	71	26	3	<1	<1	0.1
Gravel 11/22	99	65	20	2	<1	<1	<1	<1	0.1

The ferrochrome slag is hard and stable and is well suited for demanding structures. The slag products are used for road construction in the filtering and supporting layers and also as aggregate in the tarmac. Due to a smaller need of material and thus less transport during construction the ferrochrome slag products speed up the construction making the slag products economical.

2.4 Environmental qualifications of ferrochrome slag products

The grain size of the ferrochrome slag products is coarse and compared with other corresponding civil construction materials dusting is low. Very low dusting rate is demanded for a good service as insulation material. According to the standard EN 13285 fine material proportion of slag in the toughest category has to be below 3 %. In the ferrochrome slag products this measured value is below 0.5 %.

Materials that are used for civil engineering purposes have to fulfill generally the same requirements that are given for normal waste at a landfill. A proper solubility test for environmental qualifications is a column test, for which L/S 10 is used in Finland. Results of the column test for the ferrochrome slag products are shown in Table 3 and they are compared with the dumping ground requirements for permanent and usual wastes. The test results show that the slag products fulfill the dumping ground requirements in terms both the most important component chrome and the other tested metals.

Table 3: Solubility properties of the ferrochrome slag products produced by the column test L/S 10 (mg/kg)

Metal	Ferrochrome slag products	Dumping ground requirements for permanent wastes	Dumping ground requirements for usual wastes
Total chrome	0.084 - 0.112	0.5	10
Arsenic	< 0.105	0.5	2
Cadmium	< 0.011	0.04	1
Mercury	< 0.01	0.01	0.2
Fluoride	4.22 - 6.30	10	150
Molybdenum	< 0.056	0.5	10
Nickel	< 0.105	0.4	10
Zinc	< 0.941	4	50

There is little variation in the composition of the ferrochrome slag and it is well known, because FeCr and slag are analysed continuously daily in the ferrochrome process. The smelting charge is controlled both by metal and slag analyses. Metals in the slag products are scarcely soluble. According to the risk assessment carried out, concentrations of the acid-soluble components are so low that a straight contact or unintentional dilution does not produce any health hazard from metals. Structures made from the slag products are not dangerous for animals even if they drink filtered water from the structures. Soluble metals do not pollute groundwater. Extensive and long lasting medical researches have proved that long-term working within the ferrochrome products do not cause any health risks [6].

The standard leaching tests indicate only very low leaching of chrome from the ferrochrome slag. This has been proven to be a result of the mineralogical capture of chrome into the stable spinel phase and of the structural encapsulation of the dispersed crystals inside an impermeable and chemically stable glass phase [7].

The MgO and Al_2O_3 contents in the ferrochrome slag are high. Chrome oxide is bound in the spinel phases. The binding efficiency of chrome can be estimated by means of a "factor sp", which is about 30 for ferrochrome slag. If the "factor sp" is higher than 5, the solubility of chrome decreases to a very low level, Figure 7 [8]. Formation of soluble chrome salts, especially of hexavalent chrome, is implausible in the strongly reducing conditions of the smelting furnace, but chrome is trivalent or bivalent and metallic does occur. Dissolved chrome has been found to be hexavalent in standardized tests. This can be explained at least partly by variations and unknown factors in the performance of tests and analysis methods.

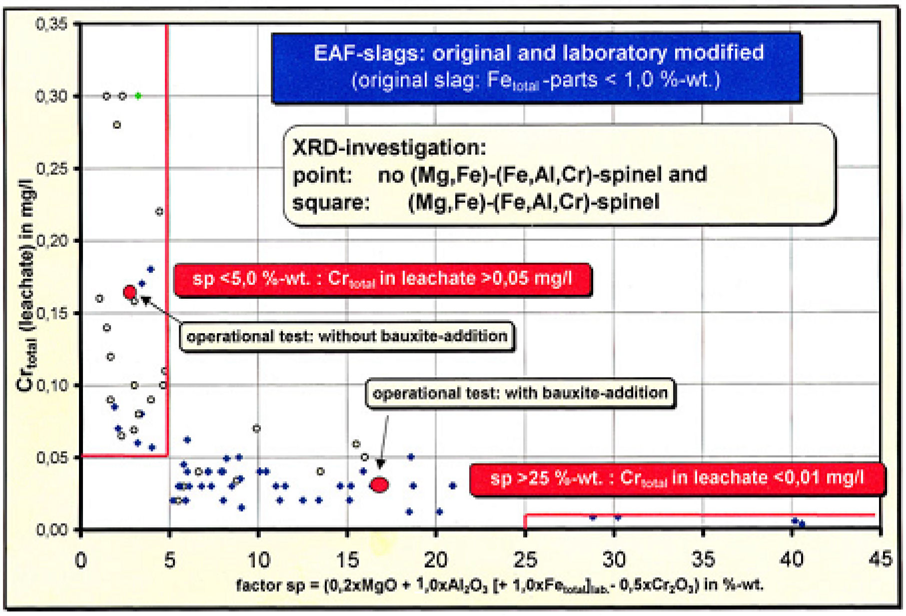

Figure 7: Dependence of Cr_{total} leachate on "factor sp"

3. CONCLUSIONS

In a large project work started by European Commission best available technology descriptions were prepared for different industry sectors. According to the results minimization of wastes, recycling of by-products, use of crushed and granulated slag for road and civil construction and also use of slag in producing refractories are described as BAT- technology [9].

The mineralogy of solid material is important when properties and environmental aspects of material are valued. The mineralogy and microstructure of the ferrochrome slag products are a reason why the chrome leaching is notably lower from the slag products than it would be expected compared with the chrome content of the slag.

The use of the industrial slag products reduces the use of natural sand and macadam. It results in positive environmental effects and that is a notable environmental aspect in the ferrochrome production. Outokumpu Tornio Works has produced over six million tonnes of ferrochrome slag during the time of operation since 1968. The ferrochrome slag products have been used in Finland since early seventies for many different purposes. No environmental disadvantages have been found because of the use. The products based on ferrochrome slag are categorized as products instead of wastes according to court proceedings. They are made as integral part of the ferrochrome production process without any material abandonment.

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