REACH REGISTRATION OF FERROUS SLAG – STATE OF THE ART

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Abstract

Since the European REACH Regulation came into force in 2007 it is compulsory for almost all marketed products to be registered according to this regulation. Given that the European steel industry always produced and sold iron and steel slag as products, those substances had to be registered under REACH. The Working Committee (WkC) of the REACH-Ferrous Slag-Consortium (RFSC), supported by the FEhS-Institute (Research Institute for iron and steel slags, Germany), external consultants and EUROSLAG (European Slag Association) has developed a dossier that allowed the successful registrations of ferrous slag as UVCB substances (Substances of Unknown or Variable Composition, Complex reaction products or Biological materials) in due time (November 2010). Meanwhile the RFSC comprises 155 plants which are concerned with the production or processing of steel and/or slag, thus representing 97% of the EU crude steel production.

Since 2010 there have been new study results included in the registrations and the Chemical Safety Report (CSR) has been revised regularly. In addition many changes in e. g. the software application (IUCLID) provided by the European Chemicals Agency (ECHA) made it necessary to update the dossiers several times. Furthermore extensive experiments were carried out and evaluated concerning e. g. possible effects by inhalation of respirable dusts. The present publication provides an overview of the state of the art in the field of ferrous slag registration.

1. Introduction/ State of the Art in 2010

The European Regulation No 1907/2006 for **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emicals (REACH) came into force on 1st June 2007 [1] and replaces a number of national regulations and directives with a single system since that time. It applies to manufacturing, import, placing on the market and use of substances, while preparations and articles do not have to be registered. Given that the European steel industry always produced and sold iron and steel slag as product or by-product, those substances had to be registered under REACH. Since the European Chemicals Agency (ECHA) had decided that, according to their developed registration tools, the group "mono-constituent/UVCB" was foreseen for slag in general, all ferrous slags were registered as UVCB substances. The following Table 1 shows the five slag families. It should be mentioned that originally all electric arc furnace slags (no. 3 and 4) were included in one family. But because of their different raw materials, this family was split into one family regarding slags from carbon steel production and one regarding slags from high alloy/stainless steel production. ECHA agreed on the separation of these slag types and accordingly the EINECS numbers were changed. No new CAS numbers were assigned.

Family no.	Substance for registration	EINECS name	Common name	EINECS no. CAS no.
1	GBS	**Slag, ferrous metal, blast furnace** (granulated)	Granulated Blast furnace Slag	266-002-0 65996-69-2
	ABS	**Slag, ferrous metal, blast furnace** (air-cooled)	Air-cooled Blast furnace Slag	266-002-0 65996-69-2
2	BOS	**Slag, steelmaking, converter**	Basic Oxygen furnace Slag (converter slag)	294-409-3 91722-09-7
3	EAF C	**Slag, steelmaking, elec. furnace** (carbon steel production)	Electric Arc Furnace slag (from Carbon steel production)	932-275-6 -
4	EAF S	**Slag, steelmaking, elec. furnace** (stainless/high alloy steel production)	Electric Arc Furnace slag (from Stainless/ high alloy steel production)	932-476-9 -
5	SMS	**Slag, steelmaking**	Steelmaking slag	266-004-1 65996-71-6

Table 1: Slag families and corresponding EINECS- and CAS-numbers

In order to get a successful registration of ferrous slag as non-hazardous in 2010, a very good knowledge of the mineralogical and the chemical composition as well as the leachability of ferrous slag was necessary. Basis for the registration work of ferrous slag was a comprehensive database which was collected by the FEhS-Institute for a long period of time. One task of the Working Committee of the REACH-Ferrous Slag-Consortium (RFSC) together with the FEhS-Institute and supported by a EUROSLAG expert group and an external consultant was to extend these data throughout Europe. Additionally to be able to work out registration dossiers, a lot of

new investigations were necessary, including special tests for possible toxicological and ecotoxicological effects. As a result, it could be shown that the behaviour of ferrous slag can be compared to natural rocks, representing an inert category of UVCB substances. Therefore, there was no need to classify them as hazardous.

2. Continuous improvement of registration

The Chemical Safety Report (CSR) has to be revised regularly, e. g. to include new study results. According to the given time frame and laboratory availability it was not possible to finalize all tests which started in 2010 or even 2009, e. g. skin irritation tests and acute inhalation tests, in time (by December 2010). The results of these tests were sent to ECHA at a later stage and were added to the CSR.

Furthermore in 2010 there was no investigation done concerning the effect of long term inhalation of respirable dust particles from ferrous slag. Meanwhile, such very time-consuming tests (in vivo and in vitro) were performed by specialised institutes [2], supported by IASON consultancy.

However, ongoing changes in the software application (IUCLID) provided by ECHA to improve the automated completeness check made it necessary to adjust the dossiers several times. The IUCLID software has been changed more than seven times up to now.

Variability is an element of the definition of UVCB substances, and this applies in particular to the chemical composition of UVCB substances. Therefore the main definition should be given e. g. by source and/or manufacture. For ferrous slag it was done by the description of the production process. According to changes in the IUCLID system, the ranges of main components contained in UVCB substances have to be included in an automatically analysable way; this applies to ferrous slag too. In any case information in the dossiers should be sufficient to allow ECHA to conclude on an unambiguous substance identity.

3. Results of ecotoxicological and toxicological investigations of ferrous slag

Based on extensive investigations ferrous slags have been registered in 2010 and classified as non-hazardous. These recognised studies included testing of possible ecotoxicological effects, e. g.:

- Growth inhibition of algae
- Short-term and long-term toxicity to invertebrates
- Effects on soil micro-organisms
- Short-term toxicity to plants

and toxicological effects, e. g.:

- Cytotoxicity studies in mammalian cells
- Gene mutation studies in mammalian cells
- Skin irritation tests
- Eye irritation tests

Additionally inhalative testing according to TRGS 430 (in combination with OECD 403) was done with ground granulated blast furnace slag (GGBS). Neither the acute test nor the post exposure period showed a toxic effect.

As a result it could be concluded from single-dose toxicity testing in animals via the oral, dermal and inhalation routes, that ferrous slag is not acute toxic. It does not need to be classified as oral, dermal and inhalation toxin; neither a signal word nor hazard statement is required. Furthermore, ferrous slag exhibits neither relevant irritant nor sensitising potential or any mutagenic potential.

But still investigations concerning repeated inhalation of fine-grained respirable dust particles from ferrous slag had to be done. The exposure by inhalation is considered to be relevant as a threshold mode of action especially for workers. GGBS is considered to cover the worst-case of ferrous slag, because it is intentionally ground for the cement industry and thus contains by far the highest amount of fine and inhalable particles compared to other types of ferrous slag.

Therefore in 2014/2015 in vivo tests were performed with GGBS which had been ground to a fineness of 4230 cm^2/g according to Blaine. All in vivo experiments were performed in Edinburgh, UK at the Charles River Laboratories Preclinical Services facility [2]. The overall design of the study was based on the study objectives, the overall safety assessment strategy for the test item, and the study design guideline OECD Guideline 412 (Repeated Dose Inhalation Toxicity: 28-Day or 14-Day Study). These inhalation studies on rats revealed that the biological responses to inhaled ferrous slag show no correlation to the course of pulmonary toxicity reported for amorphous silica (quartz). Quartz dust served as positive control as it is well known to produce irreversible lung damage. Overall, ferrous slag in vivo data differ markedly from those reported for quartz in rats exposed at similar doses.

Furthermore, in vitro tests were performed in Düsseldorf, Germany at the IUF - Leibniz Research Institute for Environmental Medicine [2], with every sort of registered ferrous slag, natural rocks and standard reference materials which served as positive or negative control, respectively. These in vitro tests also showed that ferrous slag, alike natural mineral samples, do not cause significant toxicity in cultured alveolar macrophages, nor does the slag induce major reactive oxygen species (ROS) formation and oxidative stress or trigger any inflammation in a biological system. On the contrary, the positive assay control quartz caused consistently evidence for an inflammation response in vitro associated with a significant secretion of the

mature forms of pro-inflammatory cytokines from the cells, strong activation of the inflammasome pathway, and impaired phagocytosis functionality of alveolar macrophages.

Taken together the data generated in vivo and in vitro for ferrous slag, it can be summarised that ferrous slag behaves like natural rock, representing an inert category of UVCB substances. The likely route of slags exposure is inhalation. At animal inhalation studies, no toxic effects of particular concern were observed. Results obtained from suitable in vitro studies demonstrate no certain dangerous property of ferrous slag. Finally, previous risk assessments provide sufficient supporting evidence that toxicity can reliably be excluded for ferrous slag.

The most important results of all studies on ferrous slag performed in the course of REACH registration are summarised in so called „executive summaries" on the ECHA website [3].

4. Specification of the definition of steelmaking slag (SMS)

End of 2016 ECHA got notice of the fact that separate submissions had been submitted for the same substance (Slag, steelmaking, EINECS no. 266-004-1). Examinations revealed that two slag producers coming from other industrial sectors than steel industry had registered their slags using the EINECS and CAS numbers of the steelmaking slag (SMS). Already in 2009 both companies stressed that they were very interested in joining the REACH-Ferrous Slag-Consortium as they produce slags during their processes which are, with regard to their chemical composition, similar to slags, steelmaking. The issue to participate the joint registration was discussed intensively in internal conferences and during the kick-off meeting of the RFSC in February 2009. As a result it was decided that both companies cannot participate in the joint registration due to different production processes, which is the most important defining feature.

Later on, both companies purchased a "Letter of Access" which means that they could use data, studies, summaries etc. for supporting their own registration. But according to registration rules they were not allowed to use the same EINECS number as SMS. ECHA had to generate a new one for them.

As a further result ECHA decided, that the definition of the SMS family was too broad. So RFSC had to revise the definition of the SMS family in an ambitious time frame. After intensive discussions with ECHA a new definition of SMS was generated. Now this slag family only includes slags generated during the carbon steel production process. They arise from the subsequent treatment of hot metal or of crude steel in transportable containers like ladles. Secondary metallurgical slags arising during the manufacture of stainless or high alloy steel as well as primary slags generated in electric arc furnaces or converters have been omitted from the SMS slag family. As a result, the "cloud" for SMS in the ternary diagram has been considerably reduced (s. Figure 1).

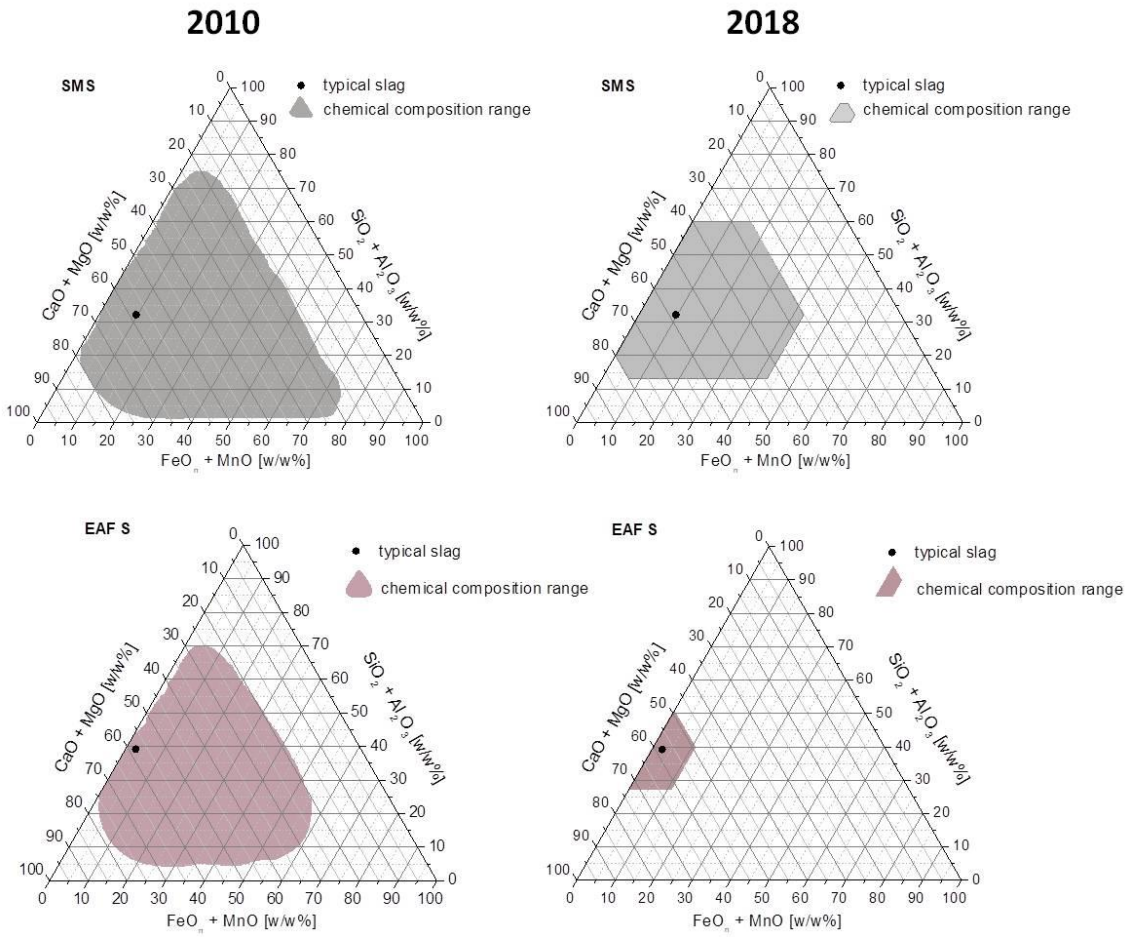

Figure 1: Ternary diagrams of SMS and EAF S; 2010 (left) und 2018 (right)

5. Chemical composition of ferrous slag

The physicochemical properties are almost identical among ferrous slags, and their benign toxicological and ecotoxicological profiles are very similar. The chemical composition varies but according to their comparable mineralogical composition they are combined in a slag category. Registrations of ferrous slag were done in 2010 as UVCB substances. The five slag families were defined mainly based on the production process and the major mineral constituents. The range of chemical composition was given by a "cloud" in a ternary phase diagram. This kind of presentation is typical for the steel industry. The composition of slag is displayed in a simplified diagram considering only those main components which form the primary mineral phases. These are (as oxides): CaO + MgO, SiO_2 + Al_2O_3 and FeO + MnO for steel slag and CaO, SiO_2, MgO + Al_2O_3 for blast furnace slag.

To be able to fulfil the request of the IUCLID system to use actual data, a new request was started in 2016 among all Consortium members who have registered ferrous slag. As a result

the data ranges of the main components for all five slag families were redefined. The major change relates to EAF S for which the "cloud" is much smaller now (Figure 1). This is due to the fact that outlier values as well as data of slag which is not marketed were eliminated.

On the basis of the survey results it was also possible to define ranges of all components with a concentration > 1 w/w% for the five slag families. Possible methods for determination of these components are XRF-analysis (e. g. EN ISO 12677) or analysis based on total digestion (e. g., EPA 3052 or EN 13211:2001) but not to aqua regia dissolution. The analytical information includes: typical concentration, lower and upper limit.

The main minerals ferrous slags are composed of are determined by X-ray diffraction. In the steel industry the analytical information on ferrous slag is usually given in the form of oxide notation although components occur in different mineral phases and different oxidation states. But the indication of all components as oxides has frequently led to problems and misunderstandings in the past. As an example, Calcium is a main component of blast furnace slag, but there is no "free" Calcium oxide (CaO), it is bound in silicates. The declaration of the Calcium content as "CaO" could be misinterpreted as being caustic lime which is classified as being hazardous. Therefore the chemical composition of ferrous slag in the registration is now given in the form of elements. As the typical concentrations have to become nearly 100 % in sum, a formula (100 - ∑ elements) is used to get the oxygen content of the slag.

6. Revision of safety data sheets

On the basis of extensive tests, ferrous slag was classified as non-hazardous in 2010. Therefore it was (and is currently) not mandatory to create a safety data sheet (SDS). But during discussions among the REACH WkC members it became clear that customers often ask for such information. Therefore draft safety data sheets were prepared by the WkC and they are called: "Material Safety Data Sheet - According to Article 32 (non-hazardous substance) Regulation (EC) No 1907/2006 (REACH)". So this is a voluntary data supply. With this action the WkC aimed at achieving a unification of the form and content of the SDSs. Those draft safety data sheets were made available to all Consortium members and they will be revised by the WkC continuously if necessary.

7. Conclusion and outlook

End of the year 2010, ECHA was provided with the registration documents for five families of ferrous slag. Meanwhile a lot of complementary investigations were performed, and the WkC of the RFSC reacted to some additional demands. In mid-2018, ECHA has accepted the revisions described before. But these were only examinations of certain parts in the dossiers. Up to now there is no evaluation of the entire registration dossiers done. That means registration dossiers will have to be refreshed regularly - and work will go on.

References

[1] Commission of the European communities, regulation (EC) no 1907/2006 of the European parliament and of the council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC,93/67/EEC, 93/105/EC and 2000/21/EC.

[2] Testing Institutes:

Charles River Laboratories Preclinical Services, Tranent (PCS-EDI) Edinburgh, EH33 2NE, UK

IUF - Leibniz Research Institute for Environmental Medicine, Auf´m Hennekamp 50, D-40225, Düsseldorf, Germany

[3] https://echa.europa.eu/de/information-on-chemicals/registered-substances