Position paper on the RIVM Report Regarding the Environmental Quality of Basic Oxygen Slag (BOS)

1. The Occasion for this Position Paper

In the Netherlands, the National Institute for Public Health and the Environment (RIVM) conducted a literature review on the environmental health quality of BOS at the request of the Environmental and Transport Inspectorate (ILT) [1]. This study was initiated by issues encountered in various projects involving steel slag. The primary objective was to gain insights into the material's environmental quality, potential risks related to its application (with a specific focus on leaching behavior), and the occurrence of carbonation.

Upon thorough examination, it becomes evident that the RIVM report includes several statements lacking scientific support or leaning towards suggestive interpretations. Additionally, the study relies exclusively on slags from India, which differ chemically from European slag. Notably, no information from Tata Steel (Netherlands) is incorporated in the literature review.

In strong opposition to the conclusions drawn in the report, we have summarized these conclusions and presented detailed responses, substantiated with supporting arguments, to express our perspective.

2. Dissecting the RIVM Report Conclusions: An evaluation and detailed response

Conclusion 1*: LD steel slag possesses hazardous properties.*

This conclusion is derived from the assumption that the slag is composed of oxides and/or hydroxides of various elements such as aluminum, calcium, chromium, phosphorus, manganese, and magnesium. It is claimed that these oxides can exhibit hazardous properties if considered as such in certain concentration. Furthermore, in the report it is claimed that the slags contain hexavalent Chromium (Cr-VI) and other heavy metals that are considered hazardous.

Response: It is crucial to highlight that considering the slags as a 'collection of individual chemicals' is entirely wrong. Oxides and heavy metals in the slag do not occur in isolated form, neither as a pure metallic element nor as a potentially harmful chemical compound. Slags are not mixtures of chemical substances. Instead, slags are complex structures consisting of individual mineral phases that interlock with each other. Similar to natural igneous rocks, these mineral phases represent the fundamental building blocks of slags. Each of these mineral phases forms a solid, crystalline structure composed of an ordered arrangement of atoms or ions. This regular structure, where atoms or ions are arranged in a repeating pattern, leads to the

formation of characteristic crystal shapes. The main elements such as oxygen, silicon, aluminium, iron, calcium, and magnesium determine the fundamental properties of a mineral, including its crystal structure and physical characteristics such as hardness, colour, and density. In addition to the main elements, minerals always contain trace and minor elements. Depending on ion size and charge, these elements can partially replace the main elements, a phenomenon known as substitution or diadochy. Due to this property, numerous trace elements are present in the slags, which do not form independent mineral phases but integrate into the structure of the emerging mineral phases. Importantly, all mineral phases of ferrous slags can also be found in natural rocks; no new component is created during steel processing.

In conclusion, it is not reasonable to designate slag as hazardous solely based on its individual constituents, which, while potentially harmful in isolation, pose no threat when bound within mineral phases. Moreover, under the REACH regulation several studies were conducted regarding potential pathways of exposure like inhalation of suspended airborne ferrous slag particles, oral ingestion of ferrous slag, and dermal contact with ferrous slag. The investigations also included the examination of ecotoxicological effects (including the hazard-relevant property HP 14 "ecotoxic" in Annex III of the EU-WFD [2]). The evaluation of these toxicological and ecotoxicological studies has shown that ferrous slags do not demonstrate any of the hazardous properties listed in Annex III of the EU-WFD - referred to as HP (Hazardous Properties). No classification according to the CLP Regulation [3] is necessary. Moreover, it's important to note that Regulation (EU) 2017/997 [4] emphasizes that assessments based on ecotoxicity tests shall take precedence over alternative approaches, such as summing up the constituents' individual ecotoxicity classifications.

The key findings of the conducted studies can be found in so-called "Executive Summaries" on the ECHA website [5] and are published in [6].

Another wrong approach in the RVIM report is to assume that chromium occurs in the hexavalent form. It is highly unlikely for several reasons that chromium is present in the hexavalent form: steel slag is a material that, despite treatment with oxygen during production, possesses reducing properties. It contains a high content of divalent iron (and it forms in an excess of metallic iron, which has strong reducing properties). Analytical results, as well as thermodynamic modelling and theoretical considerations confirm that chromium in steel slag exists exclusively in the trivalent form (e.g., 7, 8, 9, 10].

Chromium is incorporated into stable mineral phases that are resistant to weathering not soluble in water [11]. These are mineral phases that contain trivalent metals (trivalent iron or aluminium), in which the trivalent chromium takes its position during mineral formation and is

thus incorporated into the mineral structure [12]. Therefore, especially spinels, but also wuestites and calcium ferrites, can contain chromium, with spinel proving to be the main carrier [13, 14].The crystal structure of spinel ($Me^{2+}Me^{3+}{}_2O_4$) allows the incorporation of trivalent or divalent metals into the lattice sites, enabling the successful integration of chromium-III, while chromium-VI cannot be incorporated [12]. Bulk chemical analyses as well as data from the literature, including X-ray absorption near edge structure (XANES), thermodynamic modelling, and theoretical considerations, additionally confirm that chromium in steel slags exists exclusively in the trivalent form. As only the easily soluble hexavalent chromium (chromium-VI), which is not present in steel slags, is classified as toxic [15, 16, 17], from the perspective of health and environmental protection, only this species is significant. Higher concentrations of chromium (total) do not automatically pose an increased risk.

Thanks to the weathering resistance of the cited mineral phases [13, 7, 18], chromium release from SWS remains minimal. This has been studied in numerous research projects and confirmed by years of practical experience. Elution tests have consistently shown low concentrations, which align with permissible limits outlined in various regulations, even when the pH-value is modified for worst-case scenario analysis [19, 20, 21, 22]. As a result, the impact on soil and groundwater is also minimal. Furthermore, scientific research indicates that under natural conditions, no transformation occurs from chromium (III) to chromium (VI) in agricultural soils [e.g., 23, 24, 25, 26].

Conclusion 2: *The extremely high pH-value leaching and the related harmful environmental effects are an environmental problem which needs attention.*

Response: The high pH value (>11.5) of ferrous slag eluates results from the leachability of minerals containing alkali and alkaline earth metals (e.g., Ca, K, Na). According to the CLP Regulation, a substance is considered as Skin Corrosive Category 1 if it has a pH ≤ 2 or ≥ 11.5.

All tests performed for the REACH registration demonstrated that even when ferrous slag may exceed the CLP limit values for the pH-value, it does not cause a risk to human health or the environment. Additionally, it should be kept in mind that only laboratory leachates show such high pH-values. Under real conditions only a small part of alkalines is leached from the surface of the slag grains. Most of the alkaline substances is present inside the sample and mineral grains that only are destroyed when grinding the sample for the analysis in the laboratory. Under real conditions the grains are leached by water very slowly.

Furthermore, a high pH-value does not necessarily mean that a substance is irritant or corrosive. According to the CLP regulation and to the Appendix "Sequential Testing Strategy for Dermal Irritation and Corrosion - Physicochemical properties and chemical reactivity" of the Council

Regulation (EC) 440/2008, substances exhibiting pH extremes such as ≤ 2,0 and ≥ 11,5 may have strong local effects. But there is also written that the acid/alkali reserve (or buffering capacity) of the substances may also be taken into consideration if extreme pH is the basis for identifying a substance as corrosive to skin, (e. g. [27]). In case the alkaline reserve suggests that a substance may not be corrosive to the skin, then further testing should be undertaken to confirm this, preferably by the use of a validated and accepted in vitro or ex vivo test. The acid/alkali reserve referred to in the Regulation was proposed by Young et. al. (1988) [28].It represents a titration method to measure the buffering capacity by which substances may be classified as irritating or corrosive to skin.

For the registered slags, it was shown that the alkali reserve (buffer capacity) according to the method of Young et al. (1988) is < 14.5 which means that the slag leachates are not corrosive. Further laboratory tests have indicated that the tested ferrous slag does not cause skin irritation or eye damage which proves that extreme pH value alone is no sufficient indicator for corrosivity.

Conclusion 3: *The leaching of the following elements can be harmful to the environment: antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), lead (Pb), molybdenum (Mo), nickel (Ni), selenium (Se), tin (Sn), vanadium (V) and zinc (Zn). This is supplemented with anions such as: bromide, chloride, fluoride and sulfate and additionally substances such as sodium (Na), calcium (Ca), aluminium (Al), strontium (Sr), titanium (Ti), beryllium (Be) and Boron (B).*

Response: The release of most of the elements is very low and there is no anticipated environmental risk if the application is conducted appropriately and in accordance with the requirements. Furthermore, the way it is described it is suggested that because it is detected it is above a certain dangerous level. This is a false, suggestive expectation.

As explained above, the minor and trace element including heavy metals are incorporated and bound within the different mineral phases. The release of the trace elements depends on many factors, like the solubility of the particular mineral phase, pH value and grain size of the material. A general statement that the release of the listed elements is harmful is simply incorrect and cannot be accepted.

Regulations governing the use of steel slag vary across member states and depend on the application area. Usually, both technical and environmental requirements are addressed and must be met. Environmental assessment primarily involves evaluating the release or leaching of environmentally relevant elements when in contact with soil and water. Various laboratory test methods, including batch tests, column tests, or tank tests, are employed for this purpose.

The concentrations of elements in eluates must adhere to defined limit values, usually established based on scientific research. These regulations are designed to address potential environmental risks, considering a range of exposure scenarios, and ensuring the environmentally responsible use of the material.

In Germany, for instance, the Ersatzbaustoffverordnung ("Substitute Building Materials Ordinance") [29] governs the use of quality-controlled industrial aggregates, including steel slags. This regulation is based on more than 140 extensive research projects, which model substance release for various mineral construction materials under different technical applications such as roads, railroads, paved areas, excavation pits, pipe trenches, backfills, noise barriers, and visual protection walls. Compliance with specified limit values guarantees the protection of soil and groundwater, thereby demonstrating the ordinance's dedication to environmental protection.

[1] Rijksinstituut voor Volksgezondheid en Milieu (RIVM), M. Broekman (2023); Milieuhygiënische kwaliteit LD Staalslakken – Litteratuurstudie. Rapportnr 2022-0180, RIVM, Bilthoven.

[2] European Waste Framework Directive (EU-WFD); Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives (Text with EEA relevance).

[3] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

[4] Regulation (EU) 2017/997 of the Council of 8 June 2017 amending Annex III of Directive 2008/98/EC of the European Parliament and of the Council concerning hazard property HP 14 "ecotoxic".

[5] "Executive summaries" on the ECHA-Webseite. The entries can be found under the CAS- or. EINECS-No. (e.g., BOS: 294-409-3, EAF C: 932-275-6) https://echa.europa.eu/de/registration-dossier/-/registered-dossier/16150

[6] Jochims, K., Bialucha, R.: Toxicological investigations of ferrous slag in the context of the REACH registration. Report of the FEhS-Instituts für Baustoff-Forschung (2019), 33-44.

[7] Cheremisina, E., Schenk, J.: Chromium stability in steel slags. Steel Research Int. 88 (2017) 11.

[8] Lumpkin, G. R.: Crystal chemistry and durability of the spinel structure type in natural systems. Progress in Nuclear Energy 38 (2001) No. 3-13, 447-454.

[9] Chaurand, P. et al.: Environmental impacts on steel slag reused in road construction: A crystallographic and molecular (XANES) approach. Journal of Hazardous Materials (2007) Bd. B 139, 537-542.

[10] Chaurand, P. et al.: Environmental impact of steel slag reused as aggregates in road manufacturing: Molecular mechansim of chromium and vanadium Release. X-Ray Absorption Fine Structure XAF13: 13th International Conference, 9-14 July 2006.

[11] Geiseler, J., Kühn, M., Mudersbach, D.: Untersuchungen zur metallurgischen Behandlung von Schlacken aus der RSH-Stahlproduktion. Report des FEhS–Instituts für Baustoff-Forschung 6 (1999) 1, 9-11.

[12] Deer, W. A., Howie, R. A., Zussmann, J.: An introduction to the rock-forming minerals. 3rd ed., London, 2013, ISBN 978-0903056-33-5.

[13] Li, J. et al.; Effect of basicity on precipitation of spinel crystals in a CaO-SiO2-MgO-Cr2O3-FeO System. High Temp. Mater. Proc 38 (2019), 867-872.

[14] Chaurand, P. et. al.: Speciation of Cr and V within BOF steel slag reused in road constructions. Journal of Geochemical Exploration 88 (2006), 10-14.

[15] de Windt, L., Chaurand, P., Rose, J.: Kinetics of steel slag leaching. Waste Management 31 (2011) 2, 225-235.

[16] ECHA. Chromium (III) oxide. European Chemicals Agency; 2010 [updated 30 Mar 2023; cited 04 Mar 2024]. Available from: https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15477/.

[17] ECHA. Chromium trioxide. European Chemicals Agency; 2011 [updated 25 Oct 2022; cited 04 Mar 2024]. Available from: https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15927/.

[18] Lumpkin, G. R.: Crystal chemistry and durability of the spinel structure type in natural systems. Progress in Nuclear Energy 38 (2001), 447-454.

[19] Database of the FEhS-Institut für Baustoff-Forschung e.V., Duisburg, Germany.

[20] Singh, S.K., Vashistha P., Chandra R., Rai. A.K.: Study on leaching of electric arc furnace (EAF) slag for its sustainable applications as construction material. Process Safety and Environmental Protection 148 (2021) 1315–1326.

[21] Strandkvist, I., Engström, F., Palsson, K., Björkmann, B.: The influence of iron oxide on the chromium leachability of EAF slag: a full-scale study at Ovako Hofors. (2012) Scanmet IV: 4th International Conference on Process Development in Iron and Steelmaking, Luleå: MEFOS , 2012, Vol. 2, p. 329-338.

[22] Geiseler, J. und Kühn, M.: Bindung und Löslichkeit von Chrom in Düngemitteln und Baustoffen aus Eisenhüttenschlacken, FEhS-Schriftenreihe 9, 2001, pp. 65-76.

[23] ECB: European Union Risk Assessment Report chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate, potassium dichromate. 2005, 1-426.

[24] Byrne, P., Taylor, K. G., Hudson-Edwards, K. A., Barrett, J. E. S.: Speciation and potential long-term behaviour of chromium in urban sediment particulates. J Soils Sediments (2017) 17:2666-76.

[25] Kühn, M. et al. (2006): Sustainable agriculture using blast furnace and steel slags as liming agents. ECSC/RFCS Final report Project 7210-PR-267, EUR 22033 EN, 2006.

[26] Rex, M. (2002): Environmental aspects of the use iron and steel slags as agricultural lime, 3rd European Slag Conference, Keyworth, EUROSLAG Publication No. 2, 137-150.

[27] Technische Regeln für Gefahrstoffe - Einstufung und Kennzeichnung von Stoffen, Zubereitungen und Erzeugnissen (TRGS) 200, Ausgabe 2011 (http://www.baua.de).

[28] Young, J.R., How, M.J., Walker, A.P., Worth W.M.H., (1988) Classification as Corrosive or Irritant to Skin of Preparations Containing Acidic or Alkaline Substance Without Testing on Animals. Toxicology In Vitro, 27, p. 19-26.

[29] Verordnung zur Einführung einer Ersatzbaustoffverordnung, zur Neufassung der BundesBodenschutz- und Altlastenverordnung und zur Änderung der Deponieverordnung und der Gewerbeabfallverordnung V. v. 09.07.2021 BGBl. I S. 2598.