Enlightening chromium for safe circular material use in metallurgic industry with X-ray absorption spectroscopy (XAS)

INDUSTRIAL PILOT PROJECTS

THE INDUSTRIAL CHALLENGE

Developing circular economy states particular challenges for the metallurgic industry. Residual material from industrial processes shall be used in a safe way where negative effects caused by the properties of biproducts can be minimized. Slag (from HCFeCr production) as aggregate is proven to have excellent engineering properties that are beneficial in several construction applications. However, presence of Cr (VI) which has toxic properties, poses an environmental risk. Hence, in depth understanding of the oxidation state and chemical forms of Chromium (Cr), and other transition metals, is crucial to enable environmentally sound secondary use and recycling of metallurgic product residues as aggregates for construction material in bound and unbound materials for use in civil engineering work and road construction.

WHY USING A LARGE-SCALE FACILITY

Traditionally, analysis of the Cr oxidation state requires strong wet chemical pre-treatment, potentially impacting results. Furthermore, any information on the differences in the chemical form with physical location in the slag is lost. The matrix complexity in metallurgic slags poses challenges also for other traditional techniques for chemical speciation such as X-ray diffraction, also since some components in the slag is expected to be amorphous. Pre-test showed that X-ray Absorption Spectroscopy (XAS) was proven to work well for investigating chemical forms of Cr in steel slag.

HOW THE WORK WAS DONE

Samples of HCFeCr-slag, intended for recycling, were collected from various process stages (including fresh slag, slag slowly aged under environmental conditions, crushed and washed slag, as well as slag subject to accelerated aging). X-ray Absorption Near Edge Spectroscopy (XANES) was performed using the Balder beamline at MAXIV Laboratory in Lund. We targeted the typical pre-peak of Cr(VI). but also evaluated other features in the XANES spectra (energy of the absorption edge and the structures in the spectra) to gain insight in the chemical forms of Cr in the slag. High quality XANES spectra were achieved with no/minimal sample preparation, and measurements could be performed directly on solid slag samples. Collected spectra were compared to the Cr XANES spectra of selected references (15 in total), and from spectra found in the scientific literature.

THE RESULTS AND EXPECTED IMPACT

No Cr(VI) could be detected in any of the samples. This was also the case for the aged samples. Instead we could conclude that Cr primarily was found in the form of Cr(III), and in some areas also in a lower oxidation state. Mainly three chemical forms of Cr was found in the samples. At the surfaces, which had solidified in contact with air, it occurred in the form of a spinel (typically chemically stable), while other forms such as carbides were only identified in created fractures.

Figure. Slag from HCFeCr production.

Based on the results, we hypothesise that Cr(VI) is not present in the ferrochrome slag but might still be formed in contact with water. However, different chemical forms of Cr found in the slag will have different probability to form Cr(VI) in contact with water. This needs to be investigated further. Future work will include mineralogical analyses and exploring possibilities to make ferrochrome slag more resistant to environmental oxidation to Cr(VI), alternatively determine environmental conditions that prevail Cr(III) in slag recycling.

"Vargön Alloys is facing a challenging task to find environmentally friendly solution for recycling residues from the metallurgical production of high carbon ferrochromium. Using beam line technology in order to better understand fundamental properties of the slag has proven helpful." Staffan Rahmn, Vargön Alloys AB"

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