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Research of Handling of Waste, Materials and Other Products from Metallurgical and Related Process Plant

Výzkum nakládání s odpady, materiály a vedlejšími produkty hutních a souvisejících provozů

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The project is focused on research related to the possibilities of material recovery of high-volume waste products such as slags, dry and wet products from the treatment of waste gases from iron and steel production, also including products from downstream technologies such as fly ashes from power installations and solid waste products from metal casting. The project aims to generate scientific knowledge that will subsequently lead to the elimination of undesirable environmental impacts of the above-mentioned products, contribute to the increase of their material recovery and/or increase the value of the products derived from originally waste materials from metallurgical and related operations. The paper aims to present the research activities realized within the project.

***Key words**: metallurgy; slags; dusts; sludges; recovery; re-utilization of materials*

Projekt je zaměřen na výzkum možností materiálového využití vysoko objemových odpadních materiálů, jako jsou strusky, produkty mokrého a suchého čištění odpadních plynů vznikajících při výrobě oceli, dále popílky jako odpadní produkty z elektráren a rovněž odpady vznikající při tvářecích procesech. Cílem projektu je získávat vědecké znalosti, které povedou k návrhu řešení pro eliminaci nežádoucích environmentálních účinků studovaných sekundárních a odpadních materiálů, přispějí ke zvýšení jejich recyklace nebo povedou k přípravě produktů s vyšší užitnou hodnotou. Za dva roky, po které je projekt již řešen, byla prozkoumána řada materiálů vznikajících jako sekundární, nebo odpadní produkty při výrobě surového železa a ocelí. Prozatím realizované výsledky výzkumu ukazují na řadu možností využití studovaných materiálů pro přípravu produktů vysoké přidané hodnoty, jakými jsou stavební dílce připravené z alkalicky aktivovaných strusek, abraziva pro různé účely, materiály pro fotokatalytické a sorpční procesy.

***Klíčová slova**: metalurgie; strusky; popílky; kaly; recyklace; nové využití materiálů*

The main purpose of the present project is to support the enhancement of long-term inter-sectoral scientific research cooperation between the partners from research and application sectors primarily from the Ostrava agglomeration focused on the management of waste, materials and by-products originating during metallurgical and related operations. The main scientific research agenda of the project is joint research concerning the elimination, further treatment and recovery of industrial wastes, materials and by-products from metallurgical operations, which are not the primary objective of production. The project started in 2018 and 7 partners are involved in the project team: VŠB-Technical University of Ostrava, Královopolská, a.s., Liberty Ostrava a.s., Materiálový a metalurgický výzkum s.r.o., Národní strojírenský klastr, z. s., Smolo, a.s. and Třinecké železárny, a.s.

The research activities are implemented through two work packages WP1 and WP2. The research focus of both WPs is demonstrated in Fig. 1.

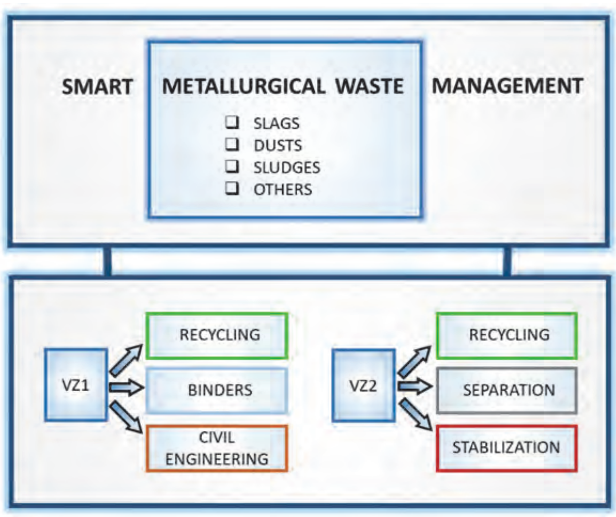

Fig. 1 Scheme of the research focus within the Work Packages WP1 and WP2

Obr. 1 Schéma výzkumu zaměřeného na tématické okruhy WP1 a WP2

Description of the work packages

The **Work Package 1 (WP1)** aims to increase the level of qualitative and quantitative material recovery of slags. Effective usage of the slags is explored and the possibilities of material recovery of slags that are not recovered yet are studied. The project involves the application of the methods of material recovery of the slags in the metallurgical industry, in the production of conventional binders, in the preparation of alternative binders by alkali activation processes, and the use of slags as the base material for civil engineering purposes. The use of slag in metallurgy assumes the search for optimal alternatives for slag recycling in melting units as well.

In the Czech Republic, iron and steel metallurgy generates more than two million tons of slag annually, with the bulk of the production being concentrated in the Ostrava region. Although there is a large part of slags, which is currently subject of material recovery, part of the slags remains unused or their recovery brings only negligible economic and social benefits. Examples include the steel slags, especially the ladle slags. Current methods of slag recovery sometimes cause problems for their users. A significant problem for the utilization of the slags is their volume instability and this problem is typical for ladle slags.

The reduction of transport and storage capacities and supporting the idea of a circular economy is one of the targets of the project. In the case of the material recovery of the slags in the production of conventional binders, the activities are aimed at researching the possibilities of slag processing in the production of Portland cement. In terms of the use of slags for the preparation of alternative binders, the possibility of preparing geopolymeric binders and low-energy types of cement is examined [1]. Concerning the use of slags as the base material (aggregates), the reasons of the volume changes of the slags and the possibility of slag treatment for suppression of this negative phenomenon is investigated [2]. These three core topics of the project are continuously enriched with new ideas including for example utilization of the slags as the abrasives [3], slags for the storage of the heat [4], slags as the raw materials for ceramic production, etc. The research activities adopted within the WP1 are schematically presented in Fig. 2.

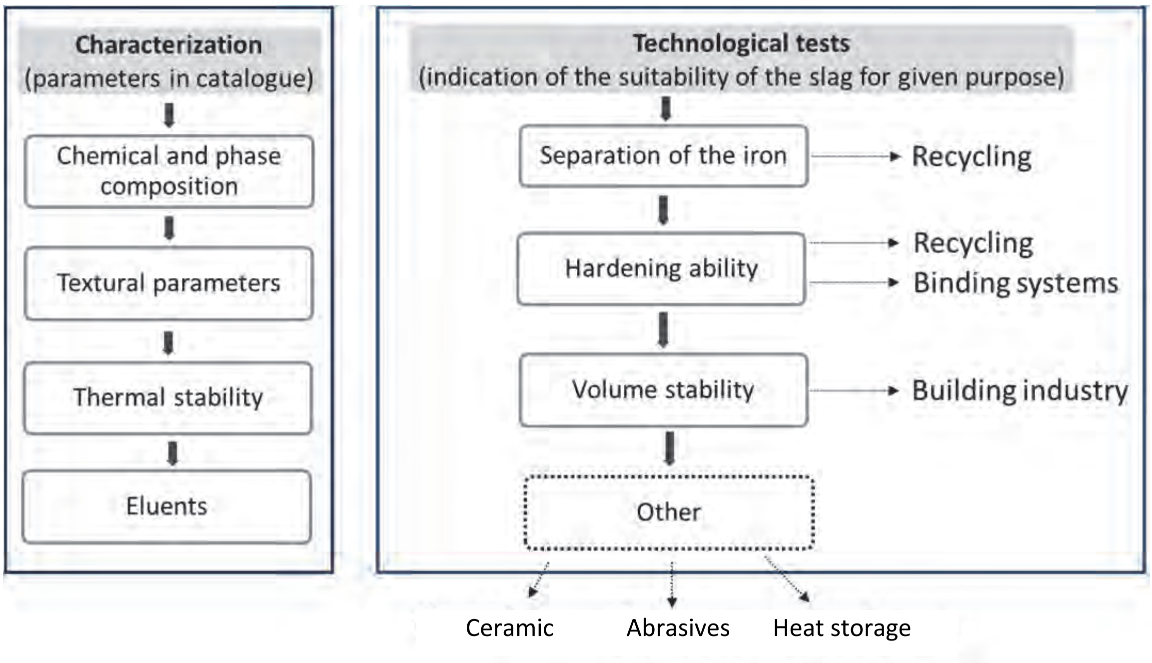

Fig. 2 Research activities adopted within WP1
Obr. 2 Výzkumné aktivity v tématickém okruhu WP1

The first part of the scheme in Fig. 2 includes the activities related to the characterization of the raw slags. The obtained parameters are collected and represent the input data for the catalogue of the slags, which is defined as one of the outputs of the project. The example of the catalogue list is shown in Fig. 3. The list contains the information about the type of the slag, its chemical composition, as well as the chemical composition and selected parameters of their water eluents. The list contains the X-ray diffraction pattern of the slag, FTIR spectra, TG and DTA curves. The ability of the slag to react with water and alkali activator is presented by the compressive strength values measured for samples after 28 days of a hydration process. The susceptibility of the slag for volume instability is also included in the list.

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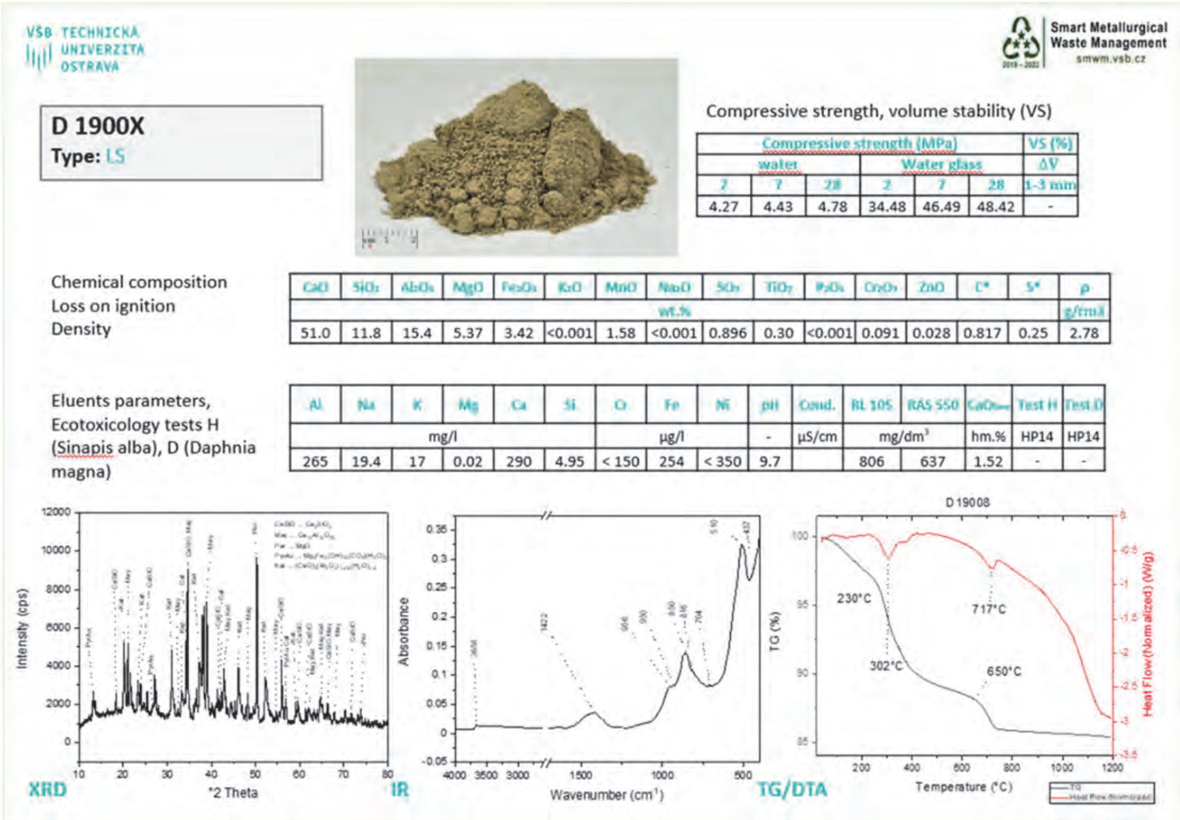

Fig. 3 Example of the list of the catalogue of the slags
Obr. 3 Příklad výpisu z katalogu strusek

The **Work Package 2 (WP2)** deals with the investigation of other solid wastes and materials, which are generated as by-products in metallurgical and related operations. The main goal is the characterization of these materials in terms of the chemical and physicochemical properties, which would lead to new and effective ways of waste treatment and thus to its recovery. Samples of a blast furnace, steel and converter sludge and various types of dust are available. These wastes arise during wet cleaning of gases from metallurgical processes, as well as by capturing of fly ash on electrostatic precipitators and fabric filters.

A high proportion of iron bounds in various oxide forms and high basicity are the characteristics of the typical sludge and dusts. Their wider recycling is hindered mainly due to the high content of zinc, or some other heavy metals. In the case of dusts from the sintering process, it is also a high content of alkalis and chlorides.

Blast furnace sludge originates during the production of pig iron in a blast furnace. It is a fine-grained material with a high weight portion of iron oxides (approximately 60 wt.%), but also with a relatively high content of heavy metals, especially zinc, cadmium and lead. These metals have low boiling points compared to the iron. In the blast furnace, they circulate in the form of vapours and condense in the colder parts of the furnace on dust particles. Zinc content may be as high as 4% in blast furnace sludge.

Steelmaking and converter sludges are generated during the production of steel in electric arc furnaces or oxygen converters. During these high-temperature steelmaking processes, iron and other accompanying elements evaporate and subsequently oxidize, while a large amount of dust particles is formed. The content of problematic heavy metals is significantly higher in these sludges in comparison with blast furnace sludges. For example, the contents of zinc in a steelmaking sludge, reach up to approximately 8 %.

The basis for the recycling of these metallurgical wastes is the separation of the iron-bearing matrix from non-ferrous heavy metals, especially zinc. Zinc separation can be achieved in two ways, by pyrometallurgical processing [5] or by hydrometallurgical processing [6 – 8]. In this work, we focused on the possibilities of hydrometallurgical processing of steelmaking sludge. It is a leaching of sludge in acid solutions. 1M hydrochloric acid and 1M acetic acid were used for the tests. The results showed comparable efficiency of both acids. 22.4 % of Zn was removed with HCl, in the case of CH_3COOH, it was 21.6 % Zn. It is relatively low efficiency. Phase analysis of original and leached steelmaking sludge (Fig. 4) revealed that zinc is present in the original sludge in two forms, zincite (ZnO) and franclinite ($ZnFe_2O_4$). While zincite dissolves well in acids, leaching of franclinite is very difficult.

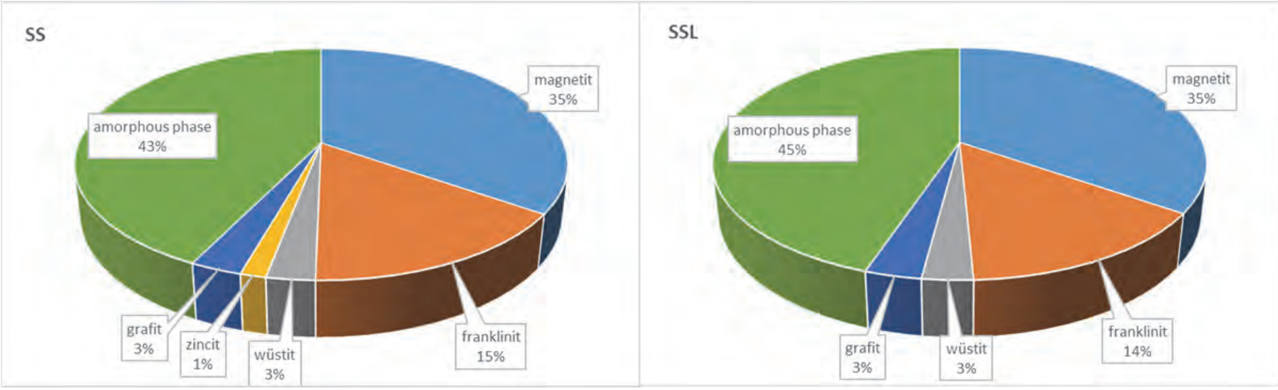

Fig. 4 Comparison of phase composition of original (SS) and leached (SSL) steelmaking sludge
Obr. 4 Porovnání fázového složení původní (SS) a louženého (SSL) ocelárenských popílků

The solid residuum obtained can be further processed in a pyrometallurgical way, for example in a rotary kiln, and subsequently returned to the metallurgical process. The reducing agent can be technical carbon mixed with the residuum or the carbon monoxide introduced into the furnace. Another possibility is the processing of solid residuum via electrochemical methods. In [9] it was shown, that during voltammetric cycling in an alkaline environment, electrode reduction of iron oxide to nanostructured Fe occurs on the surface of the leached blast furnace sludge particles. Conversely, by multiple voltammetric cycling, the surface of the sludge grains is covered with a porous nanostructured magnetite layer [10].

Acidic extracts after hydrometallurgical treatment of metallurgical sludge can, of course, be primarily used for zinc separation. There are however also other possibilities. One of them is the preparation of iron oxides, for example, hematite. For this purpose, the acidic leachate obtained using 1M HCl from the hydrometallurgical treatment of steelmaking, as well as the blast furnace sludge, were tested. As the oxidation agent, a 30% solution of H_2O_2 was used, the precipitant was a 3M solution of NaOH. The separated product was calcined at 650°C for 2 hours. The result obtained for steelmaking sludge is shown in Fig. 5. It is obvious from this figure, that hematite with an admixture of magnetite was obtained.

Acidic acetate extract containing zinc acetate as the major component is studied as a source of ZnO for the preparation of nanostructured composites based on ZnO/GO or ZnO/g-C_3N_4 with photocatalytic effects. A graphene oxide (GO) composite was prepared, and 65% of photodegradation efficiency against the model azo dye Acid Orange 7 aqueous solution was achieved.

For the above-mentioned types of metallurgical wastes, also the other possibilities of their utilisation are studied. One of them is the study related to the sorption properties of these materials. The sorption of phosphates, phenols and organic components of drugs, for example, paracetamol, is researched. Interesting results have been obtained for the oxygen converter sludge, the sorption capacities of which for phosphates are comparable to blast furnace slags and are not reduced even after the acidic leaching.

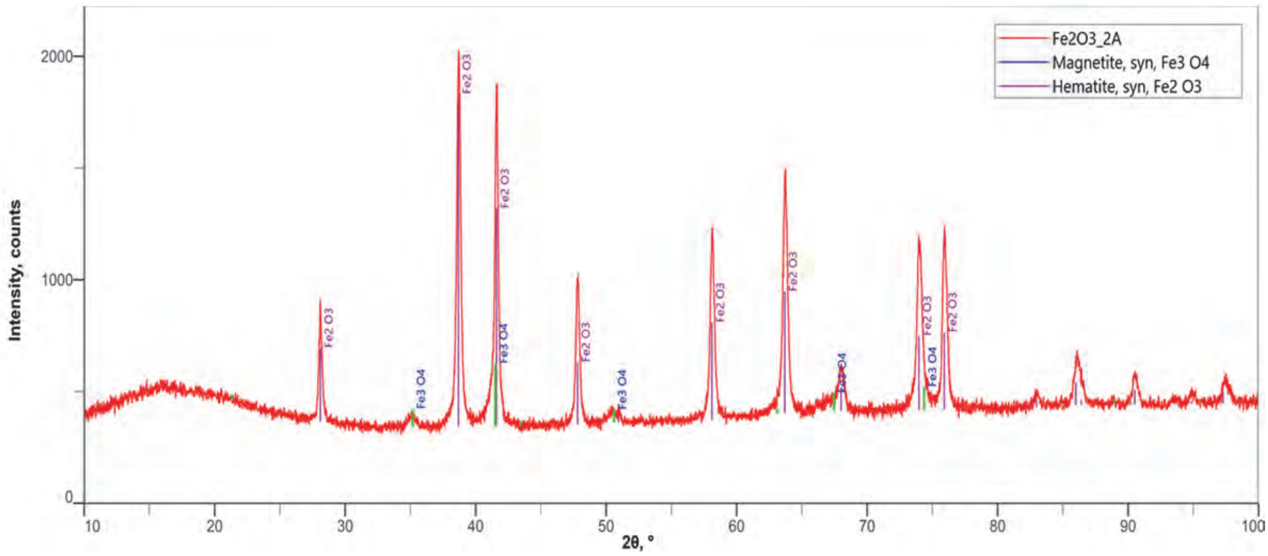

Fig. 5 X-ray diffraction pattern of calcined product
Obr. 5 Difraktogram kalcinovaného produktu

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Conclusions

The aims of both WPs´ research plans were briefly introduced in this paper. The main results coming from WP1 include the detailed characterization of prevailing types of the slags generated during the steel production, iron recycling possibilities, the ability of the parts of the slags to undergo the alkali activation process resulting in the formation of high strength products as the alternatives to construction materials based on Portland cement. The potential of the slag utilization as the abrasive was also proved within the project. The studies of the effect of the slags and their eluents on the growth of the roots of white mustard seeds and viability of Daphnia Magna indicate almost negligible impact. The WP2 aims to study and characterize waste metallurgical materials in terms of chemical and physicochemical properties, which would lead to new and effective ways of waste treatment and recovery. It is mainly the effective removal of zinc from these wastes and its further possible use, for example for the production of nanocomposites with specific properties. Solid residues after acidic leaching can be processed electrochemically, or used for sorption purposes.

Acknowledgements

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Nový velkostroj je v provozu, do ovzduší uniká méně prachu

www.trz.cz, Třinec, Tisková zpráva 16.11.2020

U zpracování surovin se v huti méně práší. Třinecké železárny dokončily jednu ze dvou investicí do dalšího snížení emisí tuhých znečišťujících látek do ovzduší. Od konce října je v provozu zařízení pro dopravu a zpětné zakládání vsázky pro výrobu ocelárenského aglomerátu.

Nový velkostroj nahradil padesát let starý portálový naběrač na homogenizační skládce. Je vybaven systémem odprášení, díky čemuž uniká do ovzduší méně prachu při zpracovávání surovin pro výrobu surového železa a oceli.

Podle propočtů jde o snížení o bezmála 60 tun ročně. 1050 tun vážící stroj je vybaven skrápěcím zařízením a odsáváním prachu z jednotlivých přesypů. Stroj nového koncepčního uspořádání umožní odběr až 1200 tun surovin za hodinu. Nyní firma staví další obdobné zařízení v bezprostřední blízkosti nového velkostroje. Ve druhém projektu jde o zařízení pro odběr a zpracování směsi pro výrobu vysokopecního aglomerátu. Zjednodušeně řečeno jde o technologii, která přepravuje suroviny nutné k výrobě surového železa. Rovněž je vybavena odsáváním prachu, díky čemuž se daří významně snížit objem prašných částic v okolí skladovacích prostor surovin, zejména rudy**.** Oba projekty huť financuje společně s prostředky z Operačního programu Životního prostředí s celkovými náklady přesahujícími 750 mil. korun.

Ekologické investice realizované v posledních letech přinesly snížení emisí prachu na historicky nejmenší objem 128 tun za rok 2019. Jde o nejmodernější zařízení svého druhu pro hutní průmysl a jsou vybaveny tkaninovými filtry, které zachytí dokonce i částice menší frakce než PM10.