Processes of Waste Recycling and Utilization in the Shaft Furnaces

Procesy recyklace a využívaní odpadů v šachtových pecích

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The production of iron and non-ferrous metals represents industries that are among the largest polluters of the environment. The production of metals is characterized by the fact that it is accompanied by large movements of raw materials and products and enormous energy consumption. This in itself poses a heavy burden on the surrounding environment, but it does not always take sufficient account of it. The inland position of our state, lacking its own raw materials and a large share of export of products adds to it. The environment is influenced by the production of metals by the widespread formation of waste products, which may be in a solid, liquid and gaseous state. In addition to direct and indirect air pollution, water and surrounding soils, the metallurgical activity affects the surrounding environment as well as noise, heat and light radiation and, last but not least, the radiation effects of some slags and other materials.

Establishing clear rules on waste management is currently determined by the relevant EU directives. In these rules, the legislation encourages the use of waste before its mere removal, particularly with regard to landfilling. These tendencies must, therefore, be part of the training of experts not only in the field of environmental protection but also in all technical fields.

***Key words**: recycling; metallic waste; shaft furnaces*

Výroba železa a neželezných kovů představuje průmyslové odvětví, které patří mezi největší znečišťovatele životního prostředí. Pro výrobu kovů je charakteristické, že je doprovázena velkými přesuny surovin a produktů a enormní spotřebou energie. To samo o sobě představuje velké zatížení pro okolní životní prostředí, ale ne vždy se dostatečně bere do úvahy. Vnitřní území našeho státu, chybějící vlastní suroviny i značný export produktů to ještě umocňuje. Životní prostředí je výrobou kovů ovlivňováno rozsáhlým vznikem odpadních produktů, které se mohou nacházet v pevném, tekutém i plynném stavu. Kromě přímého a nepřímého znečišťování ovzduší, vod a půdy ovlivňuje metalurgická činnost okolní prostředí i hlukem, tepelným a světelným zářením a v neposlední řadě i radiačními účinky některých strusek a dalších materiálů.

Stanovení jasných pravidel pro nakládání s odpady je v současnosti určeno příslušnými směrnicemi EU. V těchto pravidlech se legislativně podporuje využívání odpadů před jejich pouhým odstraněním, zejména pokud jde o ukládání na skládky. Tyto tendence musí být proto součásti i edukace odborníků nejen v oblasti ochrany životního prostředí, ale i ve všech technických oborech.

Článek předkládá kritickou analýzu a zhodnocení dosavadních výzkumných přístupů uplatňovaných při recyklaci odpadů, především z metalurgického průmyslu. I když je recyklaci odpadů v ČR i v zahraničí věnována velká pozornost, úsilí je roztříštěné a zaměřené většinou na aktuální problematiku daných regionů. Základy teorie zpracování a recyklace odpadů byly v nedávné minulosti již položeny, ale výsledky nejsou až dosud propracovány s přihlédnutím k vysokým energetickým, ekonomickým a ekologickým požadavkům na moderní alternativní technologie současnosti.

***Klíčová slova**: recyklace; kovonosný odpad; šachtové pece*

The modern method of the production of metals is distinguished by the rank of options with several differently successive, first of all, pyrometallurgical production stages where mainly carbon in various forms plays a significant role:

- such as processed black and brown coal as well as coke
- gaseous and liquid hydrocarbons occur in a large extent in waste products suitable for recycling.

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Innovations in the technologies of metal productions were mainly as follows: pre-treatment of semi-products, including desulphurization, limiting of production in the aggregates with the open hearth (production only in the oxygen converters and electric arc furnaces), separation of metal finishing from the basic smelting aggregate due to the equipment of the ladle (secondary) metallurgy, use of alternative energies (coal, oxygen, oxy-fuel burners, use of plasma technologies), as well as recyclable wastes (scrap, sludge, dusts, sinter, etc.), hydride (flexible) technological enabling operative change of composition of both charging stock and energetic inputs and this according to various criterions. Among these innovations also techniques of continuous steel production can be ranked (using EOF principle or converter). Great innovations can be represented in new products (properties orientated on using) by structural design of aggregates, in measuring sensors as well as in process models.

Metallurgical aggregates offer a unique possibility of thermal decomposition and treatment of diverse substances, which can also be applied on – currently topical – municipal waste.

A significant characteristic of high-temperature treatment processes is eliminating resources of generation of extra-hazardous furans and dioxins accompanying traditional combustion of municipal wastes in incineration plants [1 – 3].

Recycling and Waste Recycling Processes in Shaft Furnaces

Shaft metallurgical furnaces are one of the oldest technical equipment. Furnaces of this type are filled with a charge in the upper part; the charge is then falling down and has contact with hot gasses in the counter-flow. Due to charge heating through gasses, physical-chemical and chemical reactions occur. Generally, recycling of waste materials has a significant position mainly in blast-furnace technology.

Independently of using blast furnaces for recycling and exploitation of wastes also other installations based on the principle of shaft furnaces are built up, for example, processes inspired by OxyCup technology, with which the charge can consist wholly from wastes [6].

Recycling and Waste Treatment in Blast Furnaces

A great variety of technical conditions obtained in the blast furnace together with a reduction potential of the process offer a possibility of the treatment of most diverse substrates, including fly ashes. Knowledge of complex thermodynamic equilibria of reactions being in progress gives a possibility to predict quality, as well as the amount of generated products under different particular conditions of furnace work. We can also assume that in near future selected blast furnace units will be able to serve for the production of pig iron less and less and they will serve more and more as aggregates for exploitation of selected waste materials [4 – 5].

Using ferriferous waste materials as the part of blast-furnace charge offers a great spectrum of wastes, such as dust, sludge, sinter and sometimes also metallic iron in different forms. During the evaluation of the influence of these materials on the blast-furnace process as such, it is necessary to pay attention to the content of compounds and elements showing ill-effects on the process run as well as on the iron quality. It concerns first of all zinc, alkali oxides, copper, lead, tin, phosphorus, sulfur [6].

In practice, it is known that some elements and compounds occur in dangerous forms only in certain waste materials. In case of dust and sludge, it is necessary to take into account a great content of zinc, alkali compounds and lead [7 – 8].

Usual recycling procedure of these materials is realized through their batching into sinter charge. The other possible technologies of waste batching are connected with unnecessary lumping, which can be realized by various procedures.

OxyCup Process

ThyssenKrupp company together with Mannesmann Demag, Küttner companies and others have elaborated this process in the laboratory, as well as in pilot scale. Cupola with the shaft height of 5 m and hearth diameter of 2.4 m (Fig. 1) is a fundamental unit of the installation. The charge consists of briquettes in hexagon shape reaching to the height of 110 mm that are prepared from the mixture of fine-grained waste materials with addition of milled coke and cement that is used as a binding agent. An intensive reduction starts in briquette lump after heating up to 1000°C using deoxidizing agent contained in briquettes. The charge remains in blast furnace shaft for approximately 20 minutes and reduction of metal oxides occurs, as well as the beginning of charge smelting. Iron cementation takes place in blast furnace hearth.

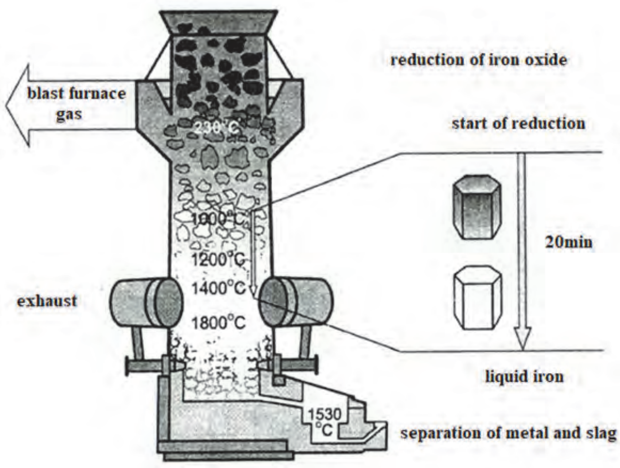

Fig. 1 OxyCup equipment scheme [6, 7]
Obr. 1 Schéma zařízení OxyCup [6, 7]

Prospective Designs of Other Blast Furnace Treatment Technologies

Requirements on properties of raw materials, especially on their grain size distribution, depend on the structural design. Beside the requirements on grain size distribution, some other requirements exist in individual cases for proper metallurgical properties of raw materials, or vice versa, these specific metallurgical properties can modify a structural solution, especially the equipment geometry. General requirement during hydrogen reduction is complying with hydrogen explosibility.

Smelting and superheating processes and the process of metal and sinter separation can be suitably connected with regard to great differences in specific gravity of iron. Connected processes require the provision of sufficient heat delivery. This can be reached provided that carbon is eliminated from the procedure either by electric current heating (inductively, by microwave radiation, by resistance, plasma or arc created among non-carbon electrodes) or by heating of reduced mixture and metal by gas, which has the necessary temperature. Nevertheless, the gas used must not have oxidizing character. The most accessible gasses in this respect seems to be nitrogen and argon, but we can also think of hydrogen [9].

The above- mentioned heating by electric current offers also various options. Heating by microwave radiation is as per nowadays knowledge accompanied by favourable secondary factors – by influencing diffusion and reduction speeding, which can markedly intensify reduction work in the zone of oxide reduction (metal generation decelerates favourable influences). This field itself, therefore, can represent one of the interesting research concentrations.

Use of carbon electrodes for heating is possible to permit in those processes where insignificant CO_2 emissions are allowed. Heating to the required temperature by gas has also some options, from using another secondary heat resource, through using electric heating up to possible use of nuclear energy [10 – 14].

During the real solution of heating for these processes, it is also necessary to solve "breathability" of smelted and separated semi-product and consequently also geometry of reaction space and heat input. For example, during blast-furnace process metallurgical coke creates frame providing breathability in the zone of softening and melting, in processes of smelting reduction it concerns usually splitting into two reaction spaces at temperatures corresponding to softening (cohesion zone) and using another type of convection to provide heat transfer (fluid, circular) in high-temperature reactor. For a new process, we can also imagine the option where breathability in lower layers (and at the same time at the highest temperatures) is provided by highly refractory ceramic balls or by another filler shape with a proper porosity [6].

Application of nitrogen, especially in combination with plasma or arc is accompanied with a risk of generation of nitrogen oxides (NO_x), therefore also their restriction, elimination, and removal have to be a part of modifications of metal (steel) production.

Alternatively, it would be possible to eliminate melting by application of chemical refining of reduced iron by the procedure of carbonyl production of powder iron, which would provide the process of metal and sinter separation. This presumes an input of metalized powdered raw material, the most optimally from the process of direct fluid reduction. Even if during production carbon monoxide is applied, it can be optimally recycled without air pollution by carbon monoxide and with limited carbonization of the final product.

Chemical refining can be also considered to be tailing extraction from ferriferous ore in the alkaline melt (for example NaOH, KOH), during which separation of particular mineralogical components occur under temperatures amounting to 350 – 450°C. These components melt to the soluble stage in the form of silicates, complex aluminates, zincates, and iron oxides. The mentioned production is based on the reversible reaction

$$Fe_{solid} + 5\ CO = Fe(CO)_5 \qquad (1)$$

In registered form reaction under the high pressure (approx. 20 MPa) and moderate temperatures (approx. 200°C) occurs. Decomposition of liquid iron pentacarbonyl occurs under atmospheric pressure, slightly increased temperatures (70 – 80°C) and permanent removal of carbon monoxide from the reaction space. Carbonization is prevented by the slight addition of ammonia and subsequent annealing of the product in a hydrogen atmosphere.

Fe hydroxides (and/or Al and other accompanying metals) can be separated from the aqueous solution and treated further on. Leach can be recycled.

A similar procedure, such as tailings extraction from iron ore in the alkaline melt is applied during production of sorbents from coal – Gravimelt Process technology (desulphurization and ash extraction). Industrial realization depends on NaOH price. The mentioned method was protected by the patent "Method of Processing Raw Materials on the basis of Oxides." Nowadays this procedure is called MLC process (molten-caustic leaching coal) [4 – 7].

For completeness´ sake, it is necessary to mention also a limited possibility of magnetic or gravity separation. With these procedures, it is possible to expect the downsizing process for achieving optimum granulometry.

The carbon-free procedure ensures production of molten pig-iron. Hydrogen and nitrogen as far as they are absorbed in steel have unfavourable effects on its properties with only minor exceptions. Therefore it is necessary to provide reaching the final steel quality by the appropriate equipment of the secondary metallurgy. From the point of view of the present state of technology development, an integral system of secondary metallurgy (ISSM) seems to be an optimum supplement enabling a majority of ladle metallurgy options.

The company VÍTKOVICE, a.s. is the licence owner and equipment producer. The principle of ISSM technology consists in secondary complex treatment of produced steel in one-reactor space where a ladle with liquid metal is placed. Generally, it includes processes of electric and chemical heating-up, alloying, carbonization, homogenization by vacuuming, degassing and sulphur removal [1].

Consequential questions are the achievement of the optimum composition of liquid metal (alloying, micro-alloying) which can be carried out either by known technologies in the equipment for secondary metallurgy or by adding an appropriate raw material into ferriferous charge under concurrent reduction of the proper element and iron.

Modification of Existing Procedures of Direct Steel Production with Plasma Burner Application

Based on previous consideration there are analyzed basic modifications of the procedures, which presume competitive steel production in comparison with existing procedures. At the same time solution of the individual critical processes should provide also minimization and/or total elimination of greenhouse gasses [4 – 7].

High consumption of energy can be justified especially in cases of processing otherwise unusable ferriferous raw materials (wastes), which require relevant refining and which cannot be processed in any other way. Efficiency can be increased by evaporated captured nonferrous metals (for example Zn, Cu, Pb). Fig. 2 shows a generalized model of plasma treatment [8 – 9].

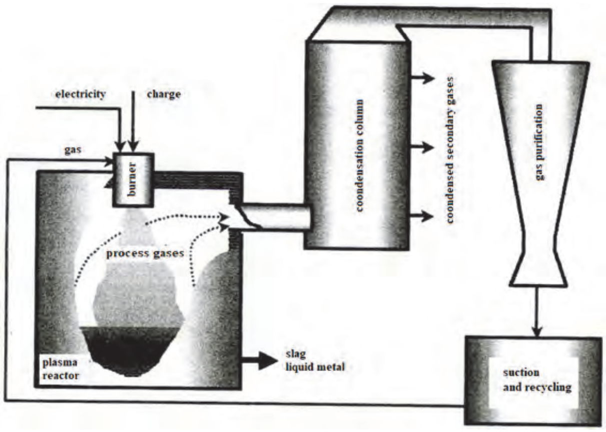

Fig. 2 Concept of plasma procedure [8]
Obr. 2 Koncept plazmového pochodu [8]

The charge would be formed by ferriferous raw material (ore, wastes) with addition agents for reaching an optimum composition of the charge mixture. Plasma is formed from any gas (Ar) enriched by a deoxidizing agent (we can think over hydrogen). Integrated processes of reduction, separation and melting are lead to the space of exhausted (vacuum treated) plasma reactor. It contains ferriferous or carbon counter-electrode where a liquid metal and sinter is collected and subsequently discharge process gasses bearing gasifying refined metals with lower melting points. Gasses leave for condensation column where they gradually condensate. Metals and/or oxides or other compounds are taken from condensation places and then transferred to another treatment. Last part of the process diagram represents the cleaning of waste gasses with the possible recycling [10 – 14].

Conclusions

In the presented study, there were carried out critical analysis and evaluation of existing research approaches applied for the recycling of waste, especially from the metallurgical industry. In conclusion it can be stated that even though great attention is paid to recycling of wastes at national, as well as foreign scope, this effort is disintegrated and usually concentrated on the topical problem of the specific region. Principles of the theory of waste treatment and recycling have been already laid in the recent past, but results have not been elaborated till now with regard to high energetic, economic and environmental requirements for modern alternative technologies of the present.

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References

[1] BROŽOVÁ, S. *Technologické, ekologické a ekonomické využití plazmy při výrobě železa a oceli.* (Dizertační práce) Ostrava: VŠB – Technická univerzita Ostrava, 2000. 88 s.

[2] HIRSCH, A., KLOCK, R., SENK, D. Vorgange in der Blasformebene von Schachtofen. In *21. Aachener Stahlkolloquium*, 14-15.9.2006, Aachen, Germany, pp. 35–45. ISBN 3-86130-906-8.

[3] SENK, D., GUDENAU, H. W., GEIMER, S., GORBUNOVA, E. Dust injection in Iron and Steel Metallurgy, *ISIJ International*, 46 (2006) 12, 1745–1751.

[4] CENGEL, P., PIVOVARČI, M. Niektoré poznatky o kontaminácii oceliarenských úletov zinkom. *Hutnicke listy*, 63 (2000) 9, 3–4. ISSN 0018-8069.

[5] BILÍK, J. Matematický model degradace koksu ve vysoké peci. *Hutnické listy*, 45 (1990) 4, 225–230. ISSN 0018-8069.

[6] LEIMALM, U., ÖKVIST, L. S., BJÖRKMAN, B. Effect of Different PCI Practice on the Texture Obtained during Reduction of Iron Oxide Pellets. *ISIJ International*, 48 (2008) 12, pp 1686–1695. ISSN 0915-1559.

[7] Ke-jiang LI, Jian-liang ZHANG, Zheng-jian LIU, Rui MAO, Tian-jun YANG. Comprehensive Evaluation of OxyCup Process for Steelmaking Dust Treatment Based on Calculation of Mass Balance and Heat Balance. *Journal of Iron and Steel Research International*. 21 (2014) 6, 575-582. ISSN 1006-706X

[8] KNEPPER, M., BABICH, A., SENK, D. Reaktionskinetic von Reduktionstragern im Hochofen und Schmelzvergaser. In *27. Aachener Stahlkolloquium*, Eurogress Aachen, Sept. 2012, pp 85–96. ISBN 978-3-941704-24-4.

[9] BARICOVÁ, D. Recycling of Oxygen Converter Flue Dust into Oxygen Converter Charge. *Metalurgija*, 41 (2002) 3, 242. ISSN 0543-5846.

[10] BROŽOVÁ, S., PUSTĚJOVSKÁ, P. Jiné možnosti zpracování kovonosných oxidických odpadů s využitím plazmového ohřevu. In *Odpadové fórum 2009*. Praha: PCHE - PetroChemEng, 2009, s. 3292–3253.

[11] PUSTĚJOVSKÁ, P., KARDAS, E., JURSOVÁ, S., INGALDI, M., BROŽOVÁ, S., KONSTANCIAK, A. Nové metody zpracování a recyklace jemnozrnných kovonosných odpadů. *Hutnické listy*, 67 (2014) 1, 24–28. ISSN 0018-8069.

[12] FINDORAK, R. et al. The Effect of Charcoal Addition on Iron-ore Sintering Emission. In. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management*, SGEM, 2, Bulgaria, 2013, pp 629–636.

[13] DŽUPKOVÁ, M., et al. Evaluation of Selected technological and Ecological Parameters of Sinter Production. *Acta Metallurgica Slovaca*, 17 (2011), 269–275.

[14] BERNASOWSKI, M. Theoretical Study of the Hydrogen Influence on Iron Oxides Reduction at the Blast Furnace Process. *Steel Research International*, Germany, 85 (2014) 4, 670–678.

Technologie HYBRIT

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Výroba oceli je energeticky velmi náročná. V současné době jsou uhlí a zemní plyn nejčastější fosilní paliva pro vytvoření vysokých teplot v tavících pecích. Švédsko zahájilo spolupráci s průmyslem na vývoji alternativy k uhlí a zemnímu plynu pro výrobu oceli. K tomuto účelu by měl sloužit vodík.

Využití vodíku může výrobu oceli zcela změnit. Základem procesu je využití energie z obnovitelných zdrojů pro výrobu vodíku a kyslíku z vody. Využitím obnovitelných energií se celý proces výroby ocelí stává téměř bezemisním. Celá technologie má název HYBRIT (Hydrogen Breakthrough Ironmaking Technology).

V červnu 2018 byl položen základní kámen pilotní ocelárny s technologií HYBRIT ve městě Luleå, které je jedním z hlavních center švédského ocelářského průmyslu. Slavnostního ceremoniálu se zúčastnil i švédský předseda vlády Stefan Löfven. Hlavními investory jsou společnosti SSAB, LKAB a Vattenfall. Dalším investorem se stala Švédská energetická agentura. Celková investice činí téměř 1,4 mld. SEK (3,46 mld. CZK). Švédska energetická agentura investuje celkem 528 mil. SEK a tři výše zmíněné soukromé společnosti celkem 830 mil. SEK. Tím se technologie HYBRIT dostává z úrovně teoretické do praxe.

Projekt získal zelenou na začátku tohoto roku a zahájení provozu se očekává na konci roku 2020. *Nová ocelárna má sloužit pouze k rozsáhlému testování a k rozvoji technologie HYBRIT, která* má zahájit ostrý provoz okolo roku 2035.

HYBRIT má potenciál snížit celkové emise oxidu uhličitého ve Švédsku o 10 % a ve Finsku o 7 %. Technologie má navíc globální potenciál snížit emise oxidu uhličitého v ocelářském průmyslu.

Mårten Görnerup, generální ředitel společnosti HYBRIT k tomu řekl:

„Zkoušení v průmyslovém měřítku je přínosnější než zkoušení v laboratorním prostředí," řekl Mårten Görnerup, generální ředitel společnosti HYBRIT.

„Umožňuje nám to přiblížit se budoucímu provozu a výrobu od začátku zefektivnit. Jsme velmi rádi, že jsme schopni přistoupit k další fázi a dostat se tak o krok blíž k našemu cíli výroby bezemisní oceli se všemi jejími přínosy pro životní prostředí.“

Za své firmy se rovněž vyjádřili přítomní hlavní investoři ze soukromého sektoru.

„Bezemisní produkce oceli začíná v dolech a LKAB intenzivně pracuje na tom, jak by měla vypadat budoucí peletizační zařízení, aby se jednalo o energeticky účinný výrobní proces," říká Jan Moström, prezident a generální ředitel společnosti LKAB. „Výzvou pro společnost LKAB v projektu HYBRIT a naším příspěvkem je vyvinout pelety s přímým snížením obsahu oxidu uhličitého. Ocelárna s technologií HYBRIT je to správné místo, kde si můžeme naše nové technologie vyzkoušet v průmyslovém měřítku.“

Martin Lindqvist, prezident a generální ředitel společnosti SSAB řekl: „Začneme-li budovat pilotní ocelárnu, kde budeme vyvíjet a rozšiřovat technologii výroby bezemisní oceli, děláme důležitý krok kupředu směrem k cíli společnosti SSAB, kterým je bezemisní výroba do roku 2045. Jsme hrdi na to, že jsme součástí důležitého a náročného technologického posunu, který může vyústit v řešení našeho klimatického problému.“

A Magnus Hall, prezident a generální ředitel společnosti Vattenfall dodává: „Vattenfall chce docílit toho, aby společnost fungovala bez fosilních paliv během jedné generace. Podpora změny výroby oceli je jedním z nejdůležitějších příspěvků, které můžeme dát. Využití elektrické energie z obnovitelných zdrojů k rozsáhlé výrobě vodíku může umožnit technické změny, které budou mít velký dopad na vznik emisí.“