Fakulta materiálov, metalurgie a recyklácie

UMET ÚSTAV METALURGIE

BÁZICKÉ ŽIAROBETÓNY – hydratácia MgO

SUČIK Gabriel, BAKAJSOVÁ Radka, POPOVIČ Ľuboš, PLEŠINGEROVÁ Beatrice, VADÁSZ Pavol
FMMR, TUKE

Abstrakt

Príspevok stručne popisuje problematiku hydratácie MgO všeobecne a jej vplyv na rýchlosť tuhnutia bázických žiarobetónov viazaných MA-sól-gél väzbou. Pre testy reaktivity boli vybrané tri typy magnézie: TS — mŕtvo pálený slinok, NED — slinutá magnézia zo soľanky a FM — tavená magnézia. Testovali sa frakcie < 80µm, 80 — 125 µm a FM 125 — 200 µm pri teplote 25 a 50 °C. Sledovala sa časová zmena pH v závislosti na type magnézie, frakcii a teplote. Pri teplote 25 °C mala najväčšiu počiatočnú rýchlosť ΔpH/s = 0.17 magnézia TS frakcie < 80 µm po 20 sekundách. Magnézie NED a FM v takom krátkom čase pH významne neovplyvnili. Magnézie boli použité pre prípravu vzoriek zmesí s prídavkom $Al_2(SO_4)_3 \cdot 18H_2O$, resp. $Al(NO_3)_3 \cdot 9H_2O$ a $MgSO_4 \cdot 7H_2O$ ako gélotvorných prísad (GP). Rýchlosť tuhnutia sa stanovovala penetračným Vicat testom. Spracovateľnosť a roztekavosť normalizovanými testami. Pilotné testy rýchlosti tuhnutia zmesí jednotlivých magnézií v kombinácií s GP ukázali na rozdiely v reológii korelujúce s ich reaktivitou a vylúčili magnéziu TS z ďalších testov. Pre ďalšie testy boli použité magnézie NED a FM s nižšou reaktivitou, no aj napriek tomu, boli rýchlosti tuhnutia bez ohľadu na typ GP vysoké (do 3 min.). Z toho dôvodu sa pri príprave žiarobetónových zmesí štandardného granulometrického zloženia postupne nahrádzali jemnozrnné frakcie inertným materiálom MA—spinelom, pričom už náhrada frakcií < 125 µm predĺžila dobu tuhnutia na 10 min. a náhrada frakcií < 500 µm na 20 minút. Ukázalo sa, že použitie magnézie TS v hrubých frakciách nad 500 µm neovplyvní rýchlosť tuhnutia. Vzorky telies z optimalizovanej bázickej zmesi boli testované na koróznu odolnosť a porovnané s korundovým žiarobetónom.

Kľúčové slová: magnézia, korund, oxid kremičitý, MA—spinel, hydratácia, sól—gél, penetrácia, korózia, pórovitosť

Spojivový systém M-A-H

Rozpustnosť v H_2O pri 20 °C		pH
$Al_2(SO_4)_3$	36.4 g/100ml	0.7
$MgSO_4$	33.7 g/100ml	5.4
Zmesný roztok 2:1		1.3

$$3MgO + 3H_2O + Al_2(SO_4)_3 \rightarrow 3MgSO_4 + 2\boldsymbol{Al(OH)_3}$$

Výpal – in situ MA-spinel

Gelácia

$$MgSO_4 + 2Al(OH)_3 \rightarrow \boldsymbol{MgO \cdot Al_2O_3} + SO_{3(g)} + 3H_2O_{(g)}$$

Chemizmus hydratácie MgO

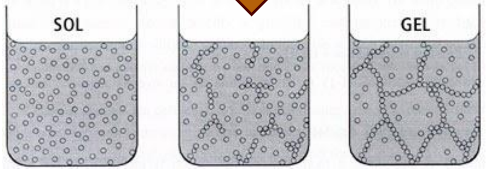
$$\boldsymbol{MgO}_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)^+_{(surf.)} + OH^-_{(aq.)} \quad (1)$$

$$[Mg(OH)]^+_{(surf.)} + OH^-_{(aq.)} \rightarrow [Mg(OH)^+ \cdot OH^-]_{(surf.)} \quad (2)$$

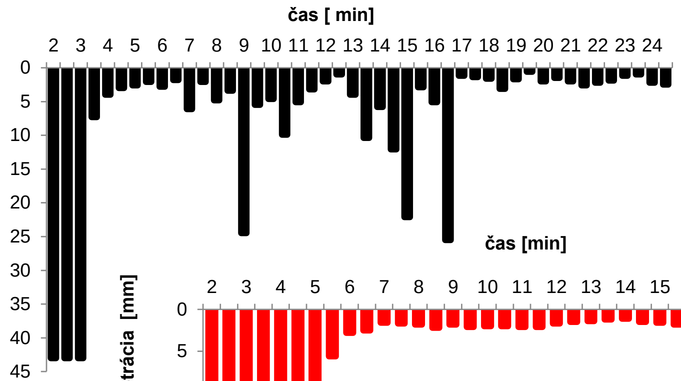
$$[Mg(OH)^+ \cdot OH^-]_{(surf.)} \rightarrow Mg^{2+}_{(aq.)} + 2OH^-_{(aq.)} \quad (3)$$

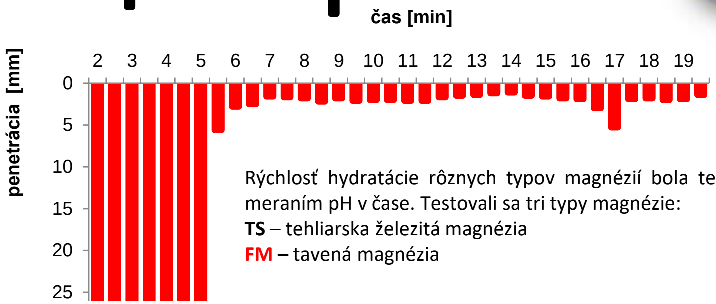
$$Mg^{2+}_{(aq.)} + 2OH^-_{(aq.)} \rightarrow \boldsymbol{Mg(OH)_{2(s)}} \quad (4)$$

MgO – nárast pH > 3

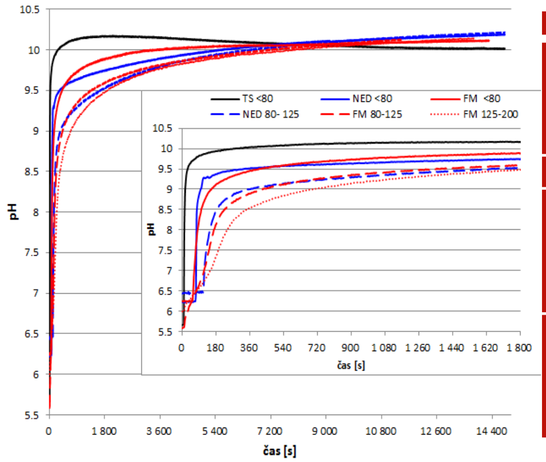


Test tuhnutia metódou VICAT





Rýchlosť hydratácie rôznych typov magnézií bola testovaná meraním pH v čase. Testovali sa tri typy magnézie:
TS – tehliarska železitá magnézia
FM – tavená magnézia



Zmena pH suspenzie MgO v závislosti na čase							
Magnézia	Frakcie	Teplota/čas					
		25 °C			50 °C		
		20 s	3 min	10 min	20 s	3 min	10 min
TS	<80 µm	9.4	9.9	10	8.8	9.2	9.3
NED	<80 µm	6.2	9.4	9.5	9.2	9.8	9.9
	80—125 µm	6.5	8.5	8.9	8.3	9.1	9.3
	125—200 µm	—	—	—	8.4	9.2	9.3
FM	<80 µm	6.3	9.1	9.4	8.6	9.2	9.3
	80—125 µm	5.9	8.2	8.8	7.8	8.7	8.8
	125—200 µm	6.2	7.4	8.4	7	8.1	8.5

Časová zmena pH suspenzie $MgO_{(s)}$ —$H_2O_{(l)}$ v závislosti od granulometrie
(Bakajsová, R., Popovič, Ľ.)

Táto práca vznikla s podporou Vedeckej grantovej agentúry MŠVVaM SR a SAV v rámci projektov VEGA 1/0060/22 a VEGA 1/0503/23.

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Analytical modelling of nitrogen content prediction in pig iron and molten steel during steelmaking process

Ing. Jaroslav Demeter, PhD.
Funded by the EU NextGenerationEU though the Recovery and Resilience plan for Slovakia under the project No. 09I03-03-V04-00047

PROJECT OBJECTIVES

This project aims to predict nitrogen content in molten metal at various steelmaking stages (pig iron, BOF/EAF crude steel, and secondary steelmaking). To achieve this, we will analyze real operational data, preprocess, synchronize, and process data. Statistical procedures will be used to develop predictive models, which will be tested and compared using machine learning techniques. The accuracy of these models will be quantified and compared to actual measurements. Additionally, analytical modeling techniques will be used to understand the relationship between factors like chemical composition, temperature, and nitrogen content. The effectiveness of the methodology will be assessed by comparing predicted and actual nitrogen values, using statistical indicators like MAE, MPE, and MAPE. The goal is to achieve high prediction accuracy within a 5-10 ppm range.

RELEVANCE, QUALITY AND NOVELTY

The current methods for predicting nitrogen content in molten metal are insufficient and rely heavily on empirical experience and traditional procedures. This often leads to suboptimal quality, especially when input materials or production processes change.

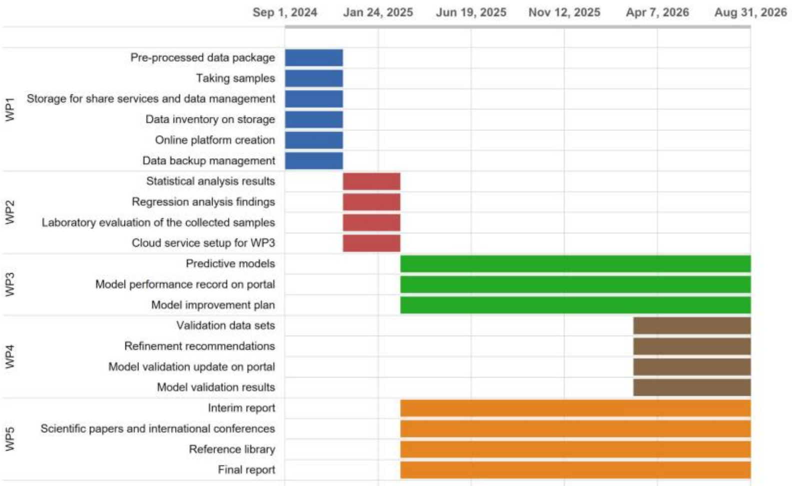
Nitrogen content is currently determined through laboratory analysis, which is time-consuming and only performed for high-quality steel grades. This delayed information hinders timely decision-making and can lead to increased nitrogen levels, negatively impacting steel properties. This project aims to address these issues by developing predictive models for nitrogen content in molten pig iron and steel. By analyzing real-time data and employing advanced statistical and analytical techniques, the models will enable accurate and timely predictions. This will significantly improve production efficiency, reduce costs, and enhance the quality of the final product. Furthermore, by aligning with the European Research Area's focus on scientific advancement and collaboration, this project contributes to the overall goal of fostering innovation and competitiveness within the steelmaking industry.

IMPACT

Predictive models are valuable tools for optimizing steelmaking processes. This project aims to develop and apply an analytical model to predict nitrogen content in molten pig iron and metal. While ambitious, the project's goals are achievable within the given timeframe.

PROJECT PLAN:

The overall structure of the submitted project plan is scheduled for 24 months. Implementation starting on 1.9.2024 and ending on 31.8.2026. Time frame for the implementation of given work packages are listed in Gantt diagram below.



For more information about this project and actual state of the solution, please log on to site:

www.nitrogen-prediction.eu

Funded by the European Union
NextGenerationEU

RECOVERY AND RESILIENCE PLAN

GOVERNMENT OFFICE OF THE SLOVAK REPUBLIC

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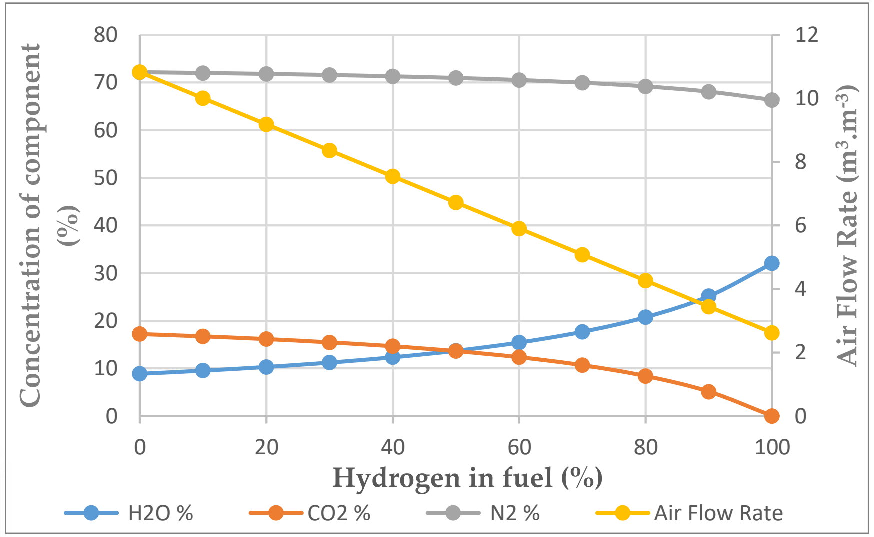
08. NOVEMBER 2024

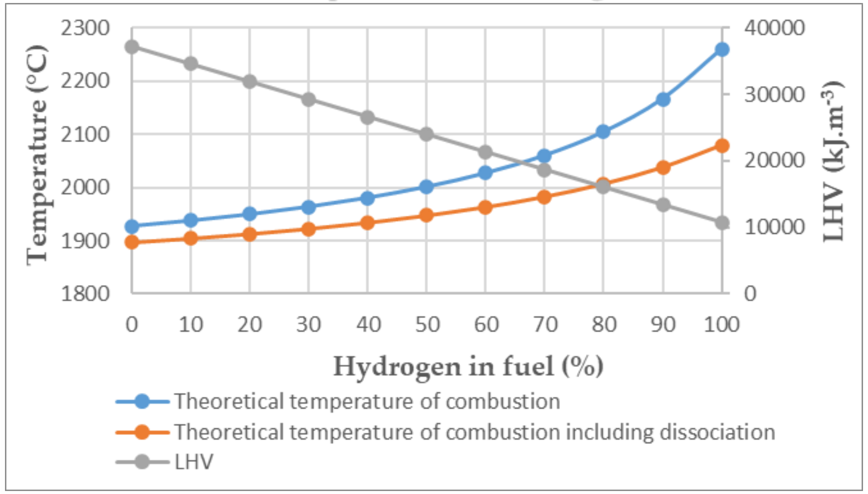
Hydrogen-Enhanced Combustion

Author: Róbert Dzurňák

Abstract:
Hydrogen-enhanced combustion is a promising approach to improve the efficiency and environmental sustainability of combustion systems. By incorporating hydrogen into traditional fuel sources, combustion characteristics change significantly, leading to a reduction in carbon dioxide emissions and increased production of water vapor as a byproduct. The enriched hydrogen content lowers air flow requirements due to reduced oxygen demand and raises the theoretical combustion temperature, which can improve thermal efficiency. Overall, hydrogen-enhanced combustion presents an effective pathway toward cleaner and more efficient energy production, but it requires careful system adjustments to safely leverage the unique properties of hydrogen.



Effect of different hydrogen concentrations in the fuel on the composition of the flue gas.



Effect of different hydrogen concentrations in the fuel on temperature and calorific value.

Acknowledgment: This research was supported by the Slovak Research and Development Agency under project number **APVV-23-0034** and the VEGA grant agency **VEGA 1/0151/2** for their financial support of this research work.

TECHNICAL UNIVERSITY OF KOŠICE,
FACULTY OF MATERIALS, METALLURGY AND RECYCLING

Fakulta materiálov, metalurgie a recyklácie

TECHNICAL UNIVERSITY OF KOŠICE
Faculty of Materials, Metallurgy and Recycling

Laboratórium testovania redukovateľnosti materiálov

Ing. Zuzana Miškovičová, PhD.

- Laboratórium na testovanie surovín (LTRM), spoločné pracovisko Technickej univerzity v Košiciach a Výskumno-inovačného centra, umožňuje výskum rudných surovín v riadenej atmosfére a teplotách.
- Zameriava sa na testovanie redukovateľnosti, objemových zmien a pevnosti materiálov, čo pomáha predikovať ich správanie v metalurgických procesoch, stabilizovať chod pecí a šetriť suroviny aj redukčné činidlá. Výsledky prispievajú k zlepšeniu ekonomiky a efektivity metalurgických podnikov.
- LTRM umožňuje testovanie nielen redukovateľnosti, ale aj napríklad objemových zmien počas ohrevu či redukcie pomocou analýzy obrazu a ďalších neštandardných metód (redukcia generovaným CO, redukcia 100% H_2).

- **zariadenie RF-33/TV/RDI**

normovaná skúška ISO 4695:2007
Stanovenie redukovateľnosti indexom redukovateľnosti

normovaná skúška ISO 7215:2007
Stanovenie relatívnej redukovateľnosti

normovaná skúška ISO 4696-1:2007
Stanovenie ukazateľov rozpadavosti po nízkoteplotnej redukcii statickými metódami (redukcia pomocou CO, CO_2, H_2 a N_2)

- **zariadenie LAC – odporová pec s retortou**

nenormované skúšky na univerzálnom pecnom zariadení,
na ktorom je možné testovať rôzne druhy materiálov,
meniť a prispôsobovať podmienky testovania
(rôzne redukčné atmosféry, teplotné podmienky, reakčné časy)

AGENTÚRA NA PODPORU VÝSKUMU A VÝVOJA

Acknowledgments: This work was supported by Slovak Research and Development Agency (APVV), Slovak Republic, No. **APVV-21-0142**

An alternative methodology for evaluating the reduction potential of BF pellets with hydrogen

Faculty of Materials, Metallurgy and Recycling

Róbert FINDORÁK

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ABSTRACT

The issue of iron production is a key issue and trends show that it will remain so for the next decades. The principle method of reduction of primary raw materials aims to use environmentally acceptable reducing agents, of which hydrogen and especially green hydrogen appear to be the most acceptable. Assessing the reduction potential of feedstocks under conditions of a hydrogen atmosphere will therefore be key for iron production, whether through a modern hydrogen blast furnace or alternative methods with this reducing agent. The paper reports on the pilot results of pellet reduction under specific conditions of 100% hydrogen in the laboratory apparatus of a tube furnace. The results of the achieved reduction stages brought knowledge about the reduction potential of the pellets and the differences in the achieved reduction stages. This new methodology makes it possible to detect the necessary differences in reducibility and, with proper validation with standard tests and relatively simple equipment, can effectively categorize individual pellets from the point of view of reducibility.

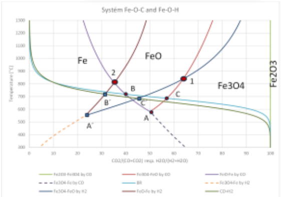
METHODOLOGY

Inputs pellets information

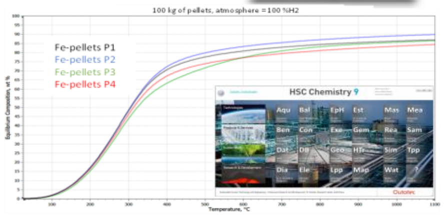
- Chemical (XRF) and phase XRD composition
- Grain size
- SEM-EDX microstructure
- Porosity
- Strength and abrasion
- Density

Prediction and simulation by

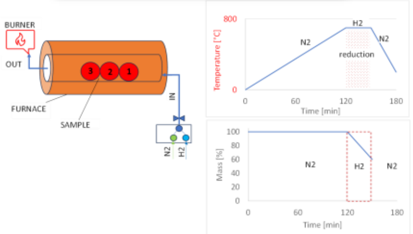
reduction theory



thermodynamicse



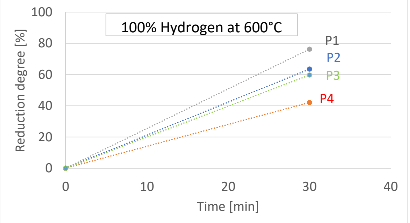
Reductin tests by H2



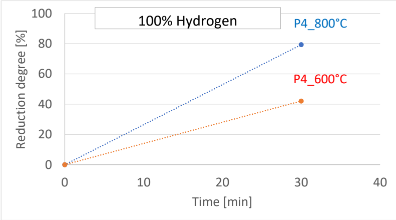
Outputs pellets after reduction

- Reduction index
- Chemical (XRF) and phase XRD composition
- SEM-EDX microstructure
- Thermal stability

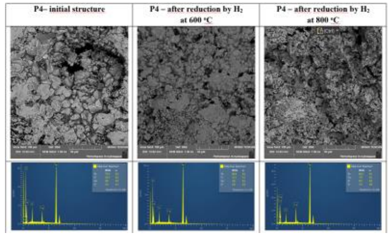
RESULTS AND CONCLUSIONS



	600°C	800°C
	Ri30 by H_2	Ri30 by H_2
P1	76.29	NA
P2	63.53	NA
P3	59.71	NA
P4	42.09	79.35



Sample	mass.% O		Loss % O	mass.% O	Loss % O
	initial	reduction at 600 °C in H_2		Reduction at 800 °C in H_2	
P1	26.5	5.2	80.4	-	-
P2	15.0	10.2	32	-	-
P3	26.4	21.6 middle / 6.7 edge	18.2 middle / 74.6 edge	-	-
P4	16.7	13.1	21.5	6.5	61.1



- Different degrees of reduction and structural changes occur at temperatures of 600 °C and 800 °C.
- A higher temperature significantly increases the rate of reduction, which is evident from the results for P4 pellets, where at 800 °C the oxygen content decreases by up to 61%.
- After reduction, the oxides are reduced to FeO and metallic iron. This process is associated with the formation of fine-grained formations and increased porosity of the structure.
- High-temperature reduction causes the formation of bright areas with significant porosity, which dominate the structure of the pellets.
- Changes in chemical composition and structure vary in different parts of the pellets.
- The results of the achieved reduction stages brought knowledge about the reduction potential of the pellets and the differences in the achieved reduction stages. This new methodology allows to detect the necessary differences in reducibility and can categorize individual pellets from the point of view of reducibility.

ACKNOWLEDGMENETS

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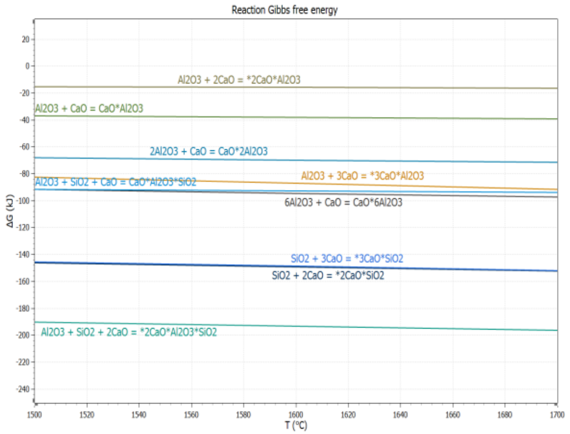
Termodynamické simulácie procesov rafinácie ocele v priebehu plynulého odlievania ocele so zameraním sa na rafinačné reakcie medzi oceľou a troskou

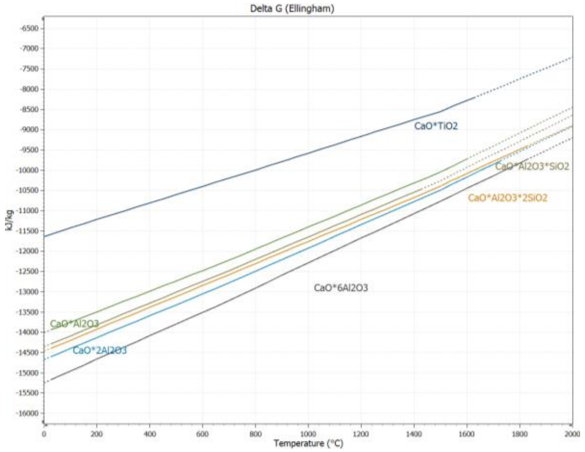
AGENTÚRA NA PODPORU VÝSKUMU A VÝVOJA

Author: Peter Demeter, Jaroslav Legemza, Branislav Buľko

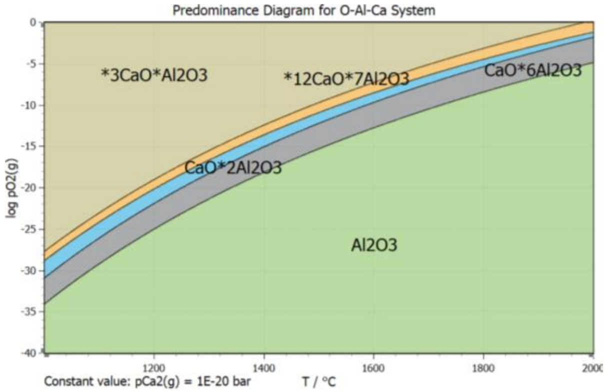
Špecifikácia systému chemických reakcií na rozhraní oceľ – troska v medzipanve



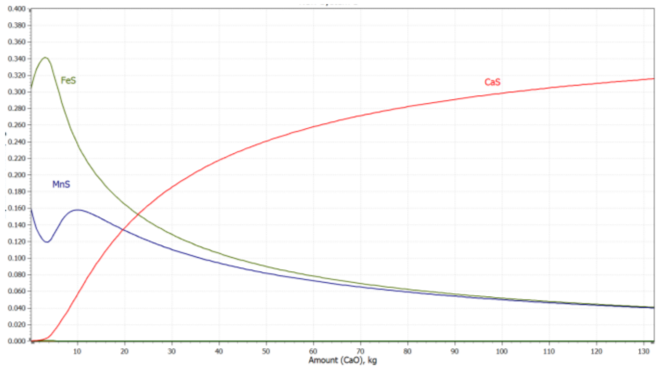
Sledovanie stability jednotlivých typov vtrúsenín – oxidov, nitridov a sulfidov



Simulácia mechanizmus vzniku a segregácie vtrúsenín v priebehu solidifikácie ocele.



Simulácia metalurgickej čistoty ocele s kontrolovaným obsahom a zložením oxidických a sulfidických vtrúsenín v priebehu plynulého odlievania ocele.



Acknowledgment: This research was supported by the Slovak Research and Development Agency under project number **APVV-21-0396** for their financial support of this research work.

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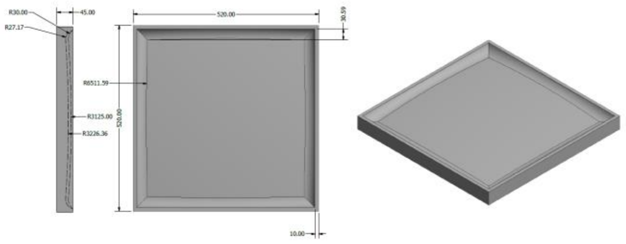
Flow pattern of liquid steel in a 4-stream ladle using a "Spheric K4" turbulence inhibitor

AGENTÚRA NA PODPORU VÝSKUMU A VÝVOJA

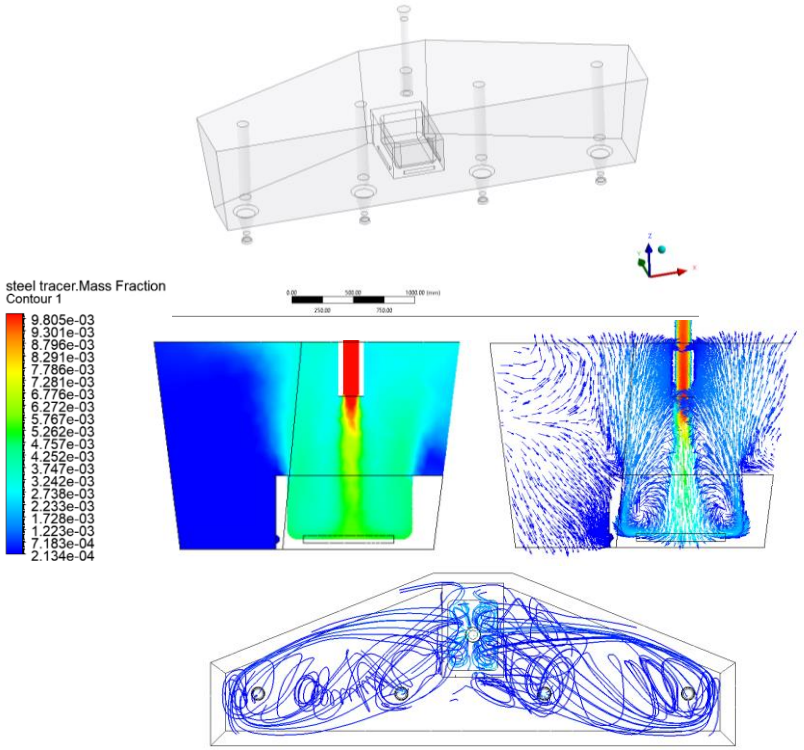
Author: Lukáš Fogaraš, Peter Demeter, Branislav Buľko

Used turbulence inhibitor

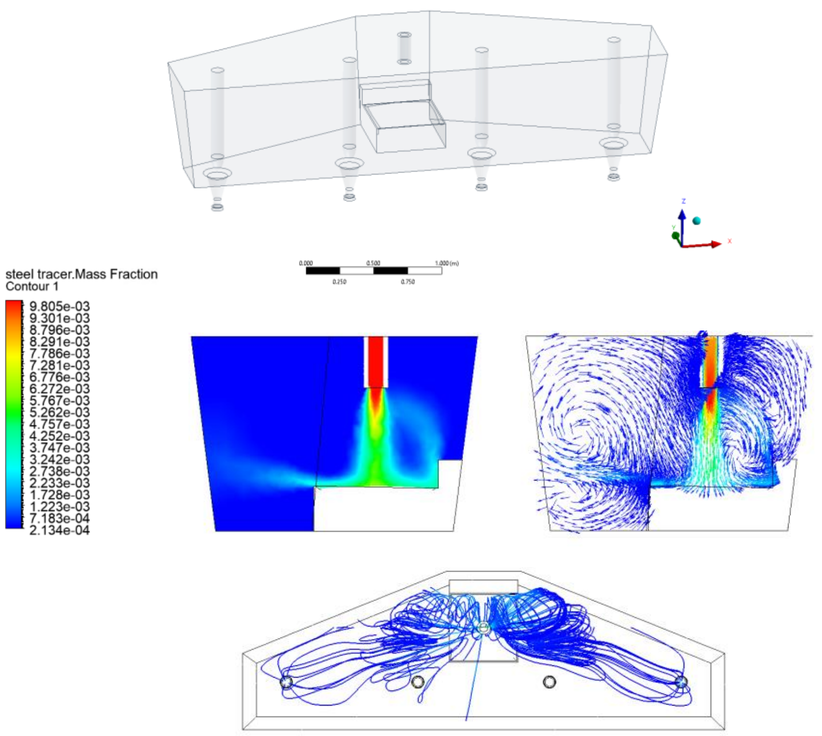


Parameter	Value
Model	
Diameter of ladle shroud [mm]	75
Depth of molten steel [mm]	825
Material	
Inlet temperature [K]	1823
Density of molten steel [kg.m-3]	7020
Viscosity of molten steel [kg.m-1.s-1]	0.0067
Specific heat[J.kg-1.K-1]	750
Thermal conductivity [w.m-1.K-1]	41
Heat flux [kw.m-2]	15
Inlet	
Mass flow Rate [kg.s-1]	27.083
Turbulent Intensity [%]	3.49
Hydraulic Diameter [m]	0.075
Outlet	
Pressure outlet	0
Turbulent Intensity [%]	5
Hydraulic Diameter [m]	0.055
Walls	
Walls (flow)	No slip
Termal Conditons [K]	1777
Wall (heat loss) [kW.m^{-2}]	2.5
Surface (heat loss) [kW.m^{-2}]	15
Tracer	
Injection time (s)	10

Reference configuration in the 4-strand tundish



Tested configuration in the 4-strand tundish



Conclusions: In the test configuration, there was a direction of the inflowing steel to the rear side, and subsequently, along the rear side, the steel was directed to the outlet strands at the end strands and then to the middle ones.

Acknowledgment: This research was supported by the Slovak Research and Development Agency under project number **APVV-21-0396** for their financial support of this research work.

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The Future of Steel: Carbon Border Adjustment Mechanisms and Its Impact by 2034

01 INTRODUCTION

The metallurgical sector is one of the main pillars of EU industry. Steel is important not only for modern economies of developed countries but is an essential part of building infrastructure in developing countries, and thus in the coming decades, global demand for steel is expected to increase to meet growing social and economic needs.

The steel industry is facing a significant challenge in reducing its carbon emissions while meeting the increasing demand for steel worldwide. To address this challenge, the industry is currently undergoing a transformation period that is evolving in two directions. The first direction is the development of completely new low-emission technologies that can potentially reduce the carbon footprint of steel production significantly. The second direction is the optimization of existing technologies to reduce their carbon emissions.

Keywords: Decarbonization, CBAM, emissions, steel industry, digitalization

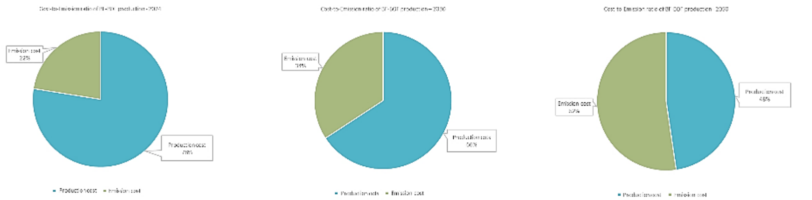
02 ECONOMIC ASSESSMENT

During the production of one ton of steel in an integrated steel plant, the direct emissions of CO2 are estimated to be in the range of 1.7 to 2.2 tons. Considering the current market price of emission permits.

The Research shows that in **2030**, emission allowances will account for **34.20%** of the total production cost of steel produced using the BF-BOF method, which is estimated at €538 per ton. By **2050**, this share will increase to **52.32%,** with the cost of steel rising to €669 per ton for the BF-BOF production process without innovation.

The high cost of emission allowances imposes additional costs on EU producers, amounting to **€200.91** per ton of steel in **2023** and **€137.14** in **2024**, with an average production of 1.91 tons of CO2 per ton of steel. During this period, the global market price for steel was €1,190 per ton of hot-rolled steel in March 2024 and €610 in August 2024, which represents the following in total costs:

In **2023**, the additional costs for emission allowances accounted for **16.89%** of the total price per ton of steel. In **2024**, these costs represented **22.48%** of the total price per ton of steel.



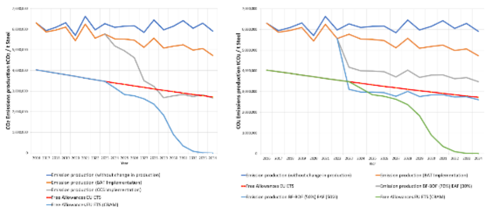
03 RESULTS

With the current exchange price of Hot-Rolled Coil steel at 850€ and the cost of the emission permit at 90€, the emissions generated during production amount to 180€ of the total production cost of the product, comprising a substantial cost that exceeds 20% of the final product's total cost.

To maintain production capacity until 2030, innovation will be incorporated into the production process through the implementation of Best Available Techniques (BATs) and CCS/CCU to optimize existing technology. This is deemed necessary due to the ongoing development phase of new low-emission technologies, which have not yet been introduced, thereby requiring a bridging period.

By utilizing modern BAT and ITs technologies, this research aims to improve the competitiveness of the steel industry by optimizing production processes and through the integration of datasets and analysis techniques contribute to reducing the carbon emissions in steel production through energy consumption optimization and the implementation of sustainable practices.

The figures show the direct carbon dioxide (CO2) emissions from steel production through two methods: integrated production using the BF-BOF process with Best Available Techniques (BAT) and Carbon Capture and Storage (left), and the transition from BF-BOF to scrap-based Electric Arc Furnace (EAF) production (right).



04 DISCUSION

➔The EU has committed to reducing emissions by 55% by 2030 compared to 1990 levels, a 15% increase from the original target set in 2014. This shift could significantly impact the steel sector, which faces long investment cycles and complex transformation processes.

➔More than **57%** of BF-BOF production plants in the EU are at risk due to rising costs of emission allowances, whose price increased from the projected **€30** to a peak of **€105.19** in March 2023 **(a rise of 250.63%)** and to **€71.8** in August 2024 **(an increase of 139.33%).**

➔The goal of the **Carbon Border Adjustment Mechanism (CBAM)** is to level the playing field between steel producers in the EU and countries with less stringent decarbonization targets. While this may enhance the competitiveness of European manufacturers, the increased emission costs could result in higher consumer prices.

05 CONCLUSION

Given the rising costs of emission allowances and their significant impact on steel production, the EU steel industry faces pressure to adapt. In the near future, these costs will represent a substantial portion of total production expenses, with emission allowances accounting for over 50% of steel prices. This places steel producers at a financial disadvantage, especially compared to regions with less stringent environmental regulations.

Furthermore, the Carbon Border Adjustment Mechanism (CBAM) offers a critical tool to offset some of the competitive disadvantages imposed by higher emission costs in the EU. However, CBAM alone will not be enough. Proactive investment in decarbonization technologies is necessary to ensure that steel producers can balance production costs while meeting the EU's ambitious climate targets for 2030 and beyond.

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