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PLENARNA PREDAVANJA

PLENARY LECTURES

Innovative solutions for the extraction of technology metals from complex primary and secondary raw materials

Željko Kamberović, Marija Korać, Zoran Anđić*

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Abstract
Technological evolution and growing demand for various high-tech devices have increased need for metals, both in terms of their diversity and quantities, resulting in more intense use of natural resources and generation of huge amounts of various waste materials. In contrast to base metals, advances in material science have given rise to a new group of metals, which are used in small or trace amounts to alter drastically the properties of matter. Whether in composite materials, like semiconductors or minor elements in alloys, these trace metals shape modern-day technology and, hence, are termed as Technology Metals (TM). Metals such as Sb, Co, Ga, Ge, In, Ta, the Platinum Group Metals (PGMs) and the Rare Earth Elements (REEs) are among the TM in which Europe is 100% import dependent. Development of the novel processing technologies will aim not only in securing raw material supply, but will rather aim to establish sustainable metallurgical processing, meaning establishing technologies for de-complexing the advanced material products with the minimum environmental footprint. Hydro and electro metallurgical steps make essential base with synergy to primary production route, advanced mechanical and minor pyro pretreatment step. However, absence of such extraction technologies, successfully applied on industrial scale, is still notable. To secure a reliable and sustainable supply of critical materials, innovative solutions need to be developed along the entire value chain. This transition requires multi-stakeholder partnerships that foster innovation and entrepreneurship, which can be obtained by applying the Triple Helix concept. Presented compilation of scientific, theoretical and experimental results, promotes an innovative synergy of various metals and industrial activities in metallurgy, resulting in profitable transformation of by-products and waste materials into resources. Focusing on treatment of specific by-products from zinc and copper primary production, as well on specific waste streams like WEEE and waste automotive catalysts, group is actively contribute to the EU sustainability policies.

1. Introduction

Usage of metals, from the earliest period of mankind history, played significant role in its development. Vast variety of applications, from water filtration systems, to modern industries like renewable energies and information technologies, best implies their significance. This booming technological evolution and growing demand in various high-tech devices have increased need for metals, both in terms of their diversity and quantities, resulting in more intense use of natural resources and generation of huge amounts of various waste materials. Unlike base metals (copper, zinc, aluminum) and iron, whose annual production only in primary sector measures in hundreds of millions of tons of metal produced, rapid development of various high-tech industries has led to the emergence of new group of metals of great importance, which are used in small or trace amounts and drastically alter the properties of materials. Whether in composite materials like semiconductors or minor elements in alloys, these trace metals shape modern-day technology and, hence, are termed as Technology Metals (TM). As a response to their importance, Commission of the European Union in 2010 launched Raw Materials Initiative, labeling 41 mineral and metals as critical material for EU, due to their direct influence on overall EU economy [1]. Among all TM, Sb, Co, Ga, Ge, In, Ta, Platinum Group Metals (PGMs) and Rare Earth Elements (REEs) are characterized with highest level of Criticality, in which Europe is 100% import dependent [2].

In last few decades, due to constant increase of metals production, enormous amounts of various waste materials are produced [3]. Some of them, even if classified as hazardous, due to presence of valuable materials, like metals, are raising a new perception to traditional concept of waste management, where these materials nowadays are classified as specific by-products rather than waste materials [4]. This is particularly important in case of historical hazardous waste materials, coming from zinc and copper primary production, landfilled in past period when companies operated using obsolete and less efficient technologies, comparing to one nowadays in use. Furthermore, materials like waste electric and electronic equipment (e-waste) or waste automotive catalysts, nowadays represents a major secondary source of base, precious and rare earth metals. All these materials, comparing to primary raw materials, contain significant amounts of TM. Therefore, their reuse and recycling has been recognized as a key factor for future sustainable development [5].

Figure 1. *Average TM content in various waste materials*

In order to secure a reliable and sustainable supply of these specific materials, innovative solutions need to be developed along the entire value chain. This transition requires multi-stakeholder partnerships that foster innovation and entrepreneurship, which can be obtained by applying the Triple Helix concept [6]. The relationships between the components of the helix concept (university-industry-government) are of crucial importance for facing the challenges coming from high process complexity and multidisciplinarity, and which individual helix components cannot resolve [7]. Moreover, implementation of helix concept is moving forward modern-day “Industrial Society” to future “Knowledge Society”, as a key respond to urgent need for more sustainable production models through sustainable mining, sustainable production and finally sustainable supply.

Therefore strategic orientations, development and implementation of novel processing technologies will aim not only in securing raw material supply, but will rather aim to establish sustainable metallurgical processing, meaning establishing technologies for de-complexing the specific advanced material products with the minimum environmental footprint. Hydro and electro metallurgical steps make essential base with synergy to primary production route, advanced mechanical and minor pyro pretreatment step. However, the relationships between the all helix components is of crucial for facing the challenges coming from the high degree of process complexity and multidisciplinary approach, resulting in notable absence of such extraction technologies successfully applied on industrial scale.

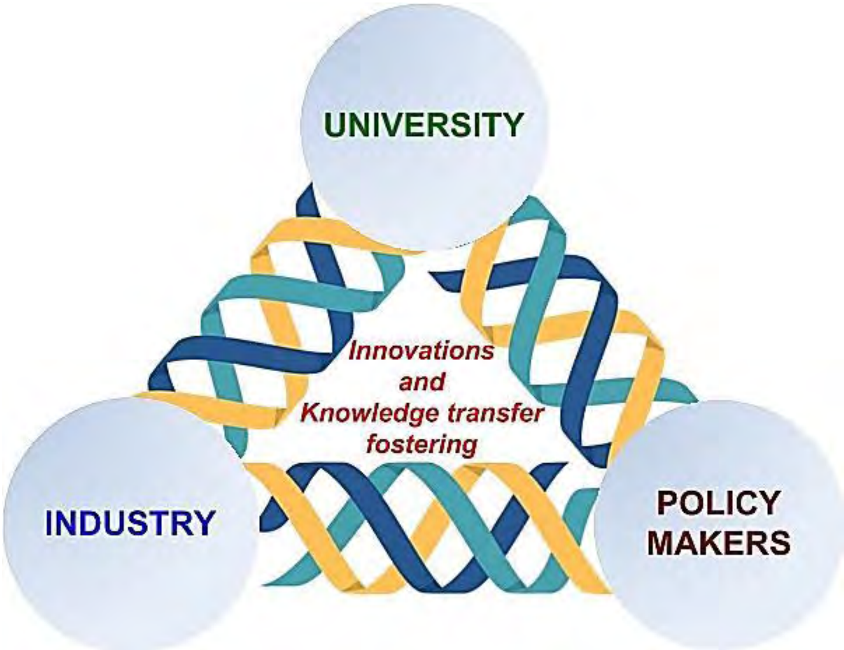

Figure 2. *Triple helix: university-industry-government relationship*

This paper presents results of various studies and projects performed by TMF Research group, as well results obtained in collaboration with complementary institutions and partners from Serbia and surrounding countries, pro-actively responding to academia responsibilities of helix concept. Effectiveness of research activities is secured by implementing methodology which may be summarized as following:

- *Parallel research:* different technologies are studied by different members, allowing an effective bottom- up approach to achieve predefined research goals;
- *Centralized Process Model:* development of a centralized process model as inter-connection of all research pathways needed for break-through technologies;
- *From Proof-of-concept to pilot:* all research activities underwent through lab scale testing and in-depth analysis of the process. Once the technological milestone for the lab scale has been achieved, scale-up will follow;
- *Down- and Up-stream industry presence*: providing the industrial partner, minimize "no-sense activities", and moreover leads to solutions with genuine market uptake potential.

Therefore, presented compilation of scientific, theoretical and experimental results, promotes an innovative synergy of various metals and industrial activities in metallurgy, resulting in profitable transformation of by-products and waste materials into resources. Focusing on treatment of specific by-products from zinc and copper primary production, as well on specific waste streams like WEEE and waste automotive catalysts, group is actively contribute to the EU sustainability policy. The overall importance of new technological concepts is reflected in new technology design, sustainable and economically justified by consideration of methods of environmental protection, which should be integrated in long-term benefit of mankind.

2.1 Waste printed circuit boards (WPCBs) recycling

Pyrometalurgical processing represents traditional and dominating method for base and precious metals recovery from WPCBs. However, low-carbon processing, in past two decades, is becoming increasingly important. Therefore, due to technological similarity of traditional hydrometallurgical methods for treatment of complex and polymetallic copper [8], zinc [9] or lead [10] bearing materials and metal-bearing wastewaters [11], most contemporary research studies are focused on implementation of analogue hydrometallurgical routes for WPCBs recycling [12]. Various studies have been reported, but generally focused on independent recovery of specific metals or metals groups, like base, precious or solder metals without investigations of compatibility and possible adverse interactions between successive leaching and recovery steps.

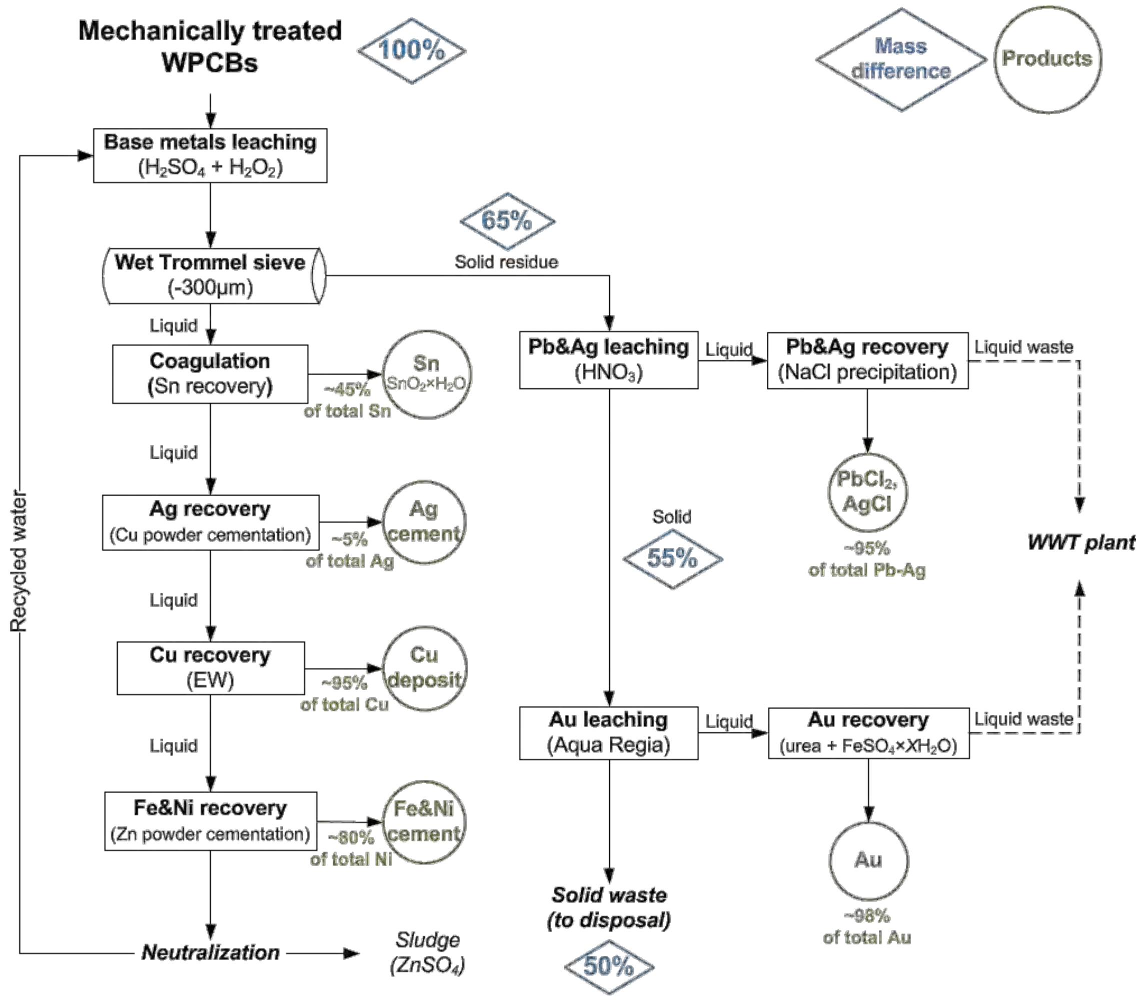

Figure 3. *Process flowsheet for integral multi-step hydrometallurgical method for selective base and precious metals recovery from WPCBs*

In this study, fully optimized technological route for selective base and precious metals recovery from WPCBs, using simple hydrometallurgical methods is presented. Full process design was performed through four phases:

- *(i)* *process modeling*: modeling and simulation was performed trough complex analysis of the system chemistry and determination of thermodynamic parameters using HSC Chemistry software.
- *(ii)* *lab-scale and pilot-scale optimization*: optimization of process parameters for each leaching and recovery step was performed trough series of lab-scale tests, investigating influence of various process parameters such as, leaching time and temperature, acid/alkali concentration and oxidizing agent addition, on overall process efficiency. Optimized processing steps were tested on pilot-scale, investigating possibility for integration in selective multi-step hydrometallurgical route for base and precious metals recovery from WPCBs.

(iii) *development of process flowsheet*: all obtained data were used for development of integrated multi-step hydrometallurgical processing route for selective base and precious metals recovery.

(iv) *preliminary techno-economic analysis*: assessment was performed using SuperPro Designer software, by simulating treatment of one tone of WPCBs trough developed hydrometallurgical route. Obtained Cost Analysis report, was used in order to determine parameters relevant for economic evaluation of process, such as costs for raw materials, utilities, labor, etc.

According to obtained results, efficiency of selective leaching and recovery of Cu, Zn, Pb, Ag and Au was above 95%, while Ni and Sn was around 80% and 45% respectively. Fully optimized hydrometallurgical route was tested on pilot scale, confirming process feasibility and allowing determination of most important parameters for development of preliminary techno-economic assessment.

Following the experimental verification of process feasibility, techno-economic assessment of proposed processing route was performed by simulating treatment of one tone of mechanically prepared WPCBs, using SuperPro Designer software. Obtained Cost Analysis report, was used in order to determine operating costs (raw materials, utilities, labor, and waste disposal costs) for treatment of one ton of WPCBs, as presented in Table 1. Within presented techno-economic assessment, total capital costs (direct and indirect) were excluded.

Table 1. *Estimated operating costs for treatment of one ton of WPCBs*

	Unit	Amount	Cost / €
Raw materials			
Sulfuric acid	L	400	120
Hydrogen peroxide	L	150	50
Hydrochloric acid	L	700	170
Nitric acid	L	700	270
Coagulant	kg	<1	10
Zn powder	kg	15	40
Cu powder	kg	1	10
Sodium chloride	kg	15	10
Ferrous sulfate	kg	1	15
Calcium hydroxide	kg	400	100
Utilities			
Water	m^3	5	10
Energy consumption	kW	450	90
Labor			
Engineering staff	h	8	50
Unskilled staff	h	18	40
Waste disposal			
Liquid waste	m^3	3	300
Solid waste	kg	700	250
Total cost			**1550**

2.2 Spent automotive catalyst recycling

Automotive catalysts contain significant amounts of platinum group metals (PGMs), dominantly Pt, but also Pd and Rh, which signifies highly efficient recycling and PGM recovery due to high value of these metals. State-of-art processes for PGM recovery from spent catalysts, involves melting of mechanically prepared spent catalysts (palletized mixture of raw catalysts, additives and metal collector), followed by electrorefining and treatment of obtained anode slime. Following the state-of-art trends, research group has successfully tested general route presented on Figure 4, on pilot scale level.

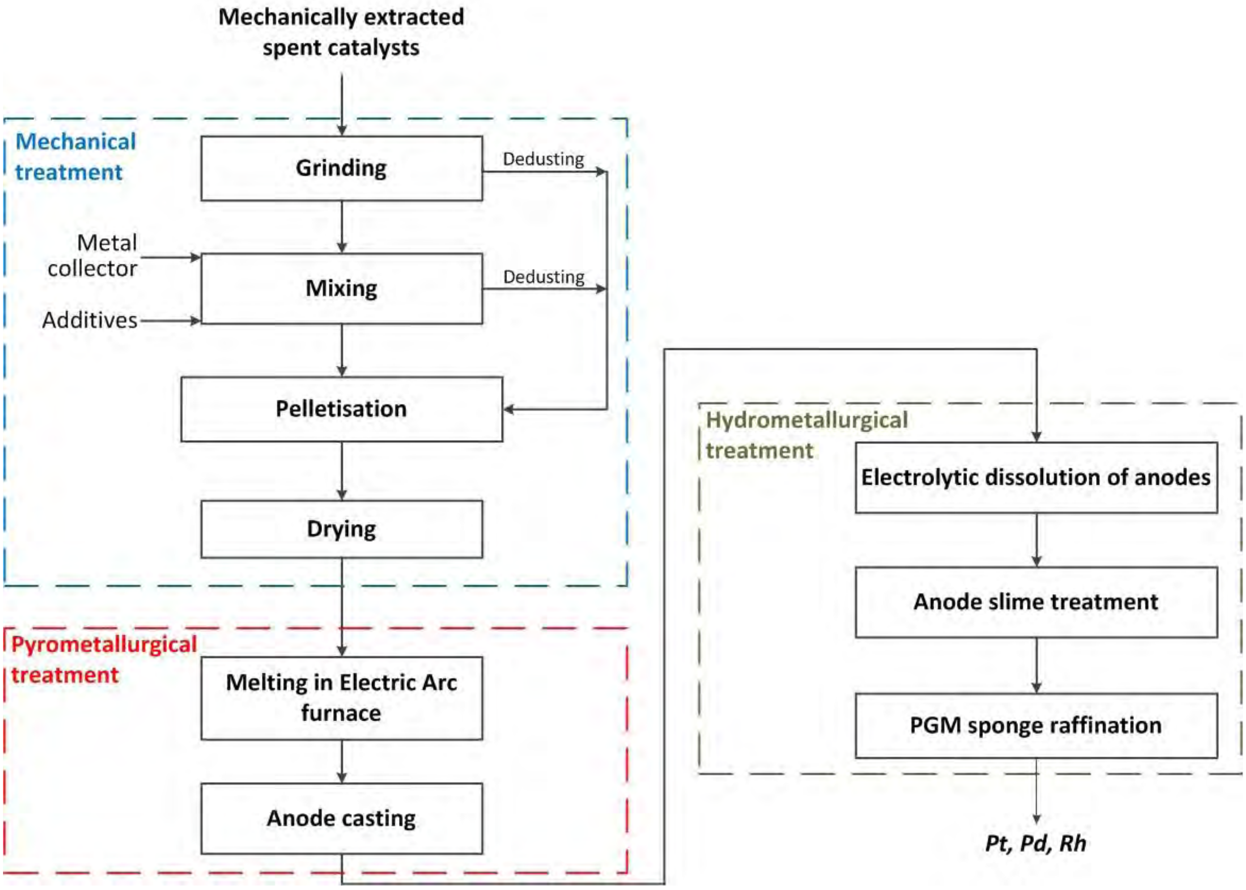

Figure 4. *Combined pyro-hydrometallurgical route for PGM recovery from spent automotive catalysts*

Material mixing and agglomeration was performed using semi-industrial pelletizing disc (Ø1000×220mm). The pelletizing disc was placed at an angle of 45° at the speed of 15min^{-1}. Milled spent catalysts, additives and Fe, as metal collector, were mixed and pelletized with lime milk suspension, as a binding agent. The produced pellets were cured at the room temperature for 2 days before further treatment. Valorisation of PGM from spent automotive catalysts was performed using semi-industrial DC plasma furnace, specially designed by ICTMF and Eling Loznica, power 100KW and 50-100 kg capacity, equipped with off gas cooling system and a bag filter, as presented on Figure 5.

Example of material balance obtained using Fe as a metal collector, containing over 94% of PGM is presented in Table 2.

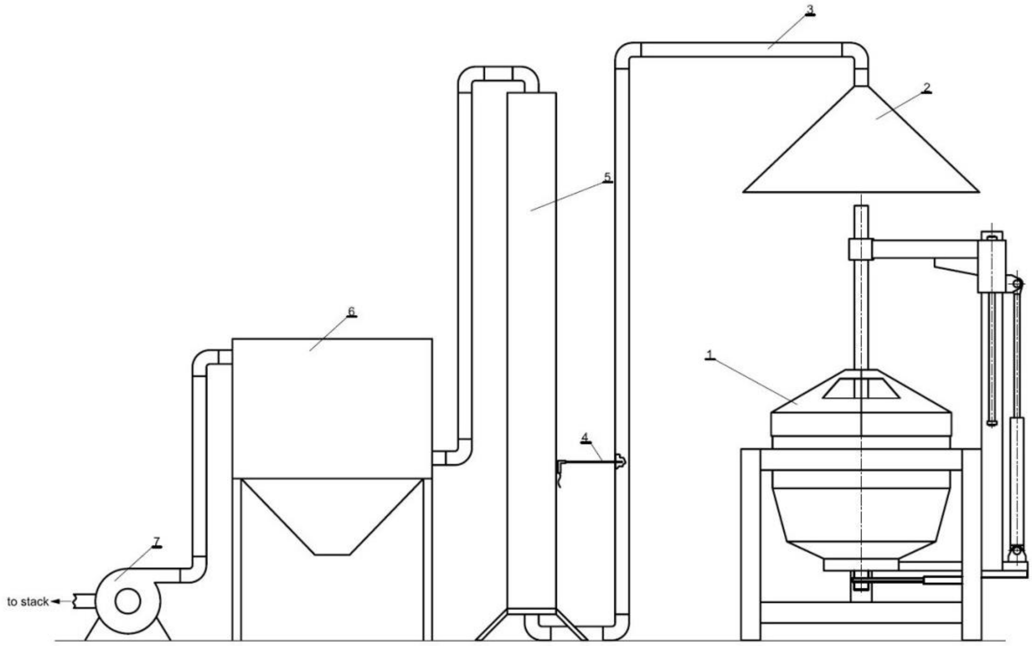

Figure 5. *Semi-industrial DC plasma furnace with a gas cooling system and a bag filter: 1 DC plasma furnace, 2. Hood, 3. Off-gas pipeline, 4. Off- gas quality measuring, 5.Cooling tower, 6.Bag filter, 7. Fan*

Table 2. *Material balance obtained using Fe as a metal collector*

Input	g	% cat.	kg/t cat.
Spent catalysts	13.790	100.0	1.000
Aditive-01 (lime-coke$_{7\%}$)	1.032	7.5	75
Aditive-02 (mill scale Fe$_{70\%}$)	480	3.5	35
Aditive-03 (hydrated lime)	900	6.5	65
Aditive-04 (Fe$_{99\%}$)	900	6.5	65
Aditive-05 (Fe cutting scrap)	500	3.6	36
PSC slag	50	0.4	4
Total	17.652	128.0	1.280
Output			
Metal	1.904	13.8	138
Plasma slag	12.455	90.3	903
Filter products	108	0.8	8
Deposit	40	0.3	3
Total	14.507	105.2	1.052
Weight loss	3.145	22.8	228

2.3 Copper primary production by-products treatment

As stated, historical waste materials coming from primary production sectors nowadays represent specific by-products suitable for valorization of valuable materials contained within. In primary copper production, huge amounts of mines overburden and wastewater from smelters are generated. Aside from being an environmental problem, overburden should be treated in terms of copper recovery. Overburden from Cerovo mine, Bor, is assessed at around 25 million tons with an average copper content of 0.18-0.21% and estimated theoretical value of 300.6 million US$ [13,14]. In overburden, copper is mostly present in the form of oxide ore. Hydrometallurgical methods (crushing and leaching, followed by solvent extraction (SX) and electrowinning (EW)) are usually applied for processing of low grade oxide ores [14,15]. Wastewater from copper smelter is generated during the treatment of SO_2 gas and flue dust in wet scrubbers. Projected amount of wastewater from New copper smelter RTB Bor is 8.66 m^3/h, very acidic, containing 142.7 g/L of H_2SO_4 and 0.53 g/L of dissolved copper [16]. Best available technique for the treatment of wastewater from primary copper production is acid neutralization and metals ion precipitation in the form of hydroxides by using hydrated lime ($Ca(OH)_2$). This is a widely used method due to low prices and high lime efficiency. However, main disadvantage of this method is formation of large amounts of hazardous WWT sludge that requires treatment prior disposal [17,18].

Within the scope of treatment of specific by-products coming from copper primary production, research group has developed an integral treatment of copper mine overburden and copper production effluents from Mining and smelting combine Bor. Integral treatment includes neutralization of acidic wastewater from copper smelter using overburden from Cerovo mine simultaneously leaching copper from oxide ore, with aim to obtain solution suitable for copper recovery by SX/EW process.

Process of acid neutralization/copper leaching was investigated by simulation in SuperPro Designer program combined with HSC Chemistry software.

The main constituents of overburden from Cerovo, as well projected characteristics of wastewater generated in New copper smelter RTB Bor are presented in Table 3 and 4.

Table 3. *Main constituents of overburden from Cerovo*

Component	**%**
$SiO_2 + Al_2O_3$	75.6
Fe (as oxides)	5.3
Fe (as sulphides)	3.5
Cu (as oxides)	0.16
Cu (as sulphides)	0.11
Carbonates	14.5

Table 4. *Copper smelter wastewater characteristics*

	Unit	Value
Temperature	^oC	55
Volume	m^3/h	8.66
Density	t/m^3	1.069
Solids content	%wt	1.36
Acid content (H_2SO_4)	g/L	142.7
pH		-0.464
Dissolved metals		
Cu	g/L	0.53
Fe^{2+}	g/L	0.38
Zn	g/L	0.54
Pb	g/L	0.45
As	g/L	1.37

Simulation of the acid neutralization/copper leaching process is performed using SuperPro Designer software combined with thermodynamics data obtained in HSC Chemistry software. Simulation parameters are set to obtain solution with pH=2. Possible reactions during the process with thermodynamic parameters at 50°C are presented in Table 5.

Table 5. *Reactions in acid neutralization/copper leaching process*

Reaction	ΔH, kJ	ΔS, J/K	ΔG, kJ
$CuO + 2H^{+} + SO_4^{-2} = Cu^{+2} + SO_4^{-2} + H_2O$	-64.402	-68.449	-42.283
$Fe_2O_3 + 6H^{+} + 3SO_4^{-2} = 2Fe^{+3} + 3SO_4^{-2} + 3H_2O$	-134.115	-433.851	6.084
$CaCO_3 + 2H+ + SO_4^{-2} = Ca^{+2} + SO_4^{-2} + CO_2(g) + H_2O$	-15.857	135.403	-59.612
$MgCO_3 + 2H+ + SO_4^{-2} = Mg^{+2} + SO_4^{-2} + CO_2(g) + H_2O$	-49.787	83.390	-76.734
$Na_2CO_3 + 2H+ + SO_4^{-2} = 2Na^{+} + SO_4^{-2} + CO_2(g) + H_2O$	-26.963	268.842	-113.839

Characteristics of solution resulted from acid neutralization/copper leaching process, as an outflow from simulation, is presented in Table 6.

Table 6. *Characteristics of solution after acid neutralization/copper leaching*

Characteristics of solution	Unit	Value	Dissolved metals	Unit	Value
Volume	m^3/h	8.79	Cu	g/L	1.68
Density	t/m^3	1.192	Fe^{2+}	g/L	0.81
Acid content (H_2SO_4)	g/L	0.63	Zn	g/L	0.96
pH		2.00	Pb	g/L	0.51
			As	g/L	1.44

Simulation results show that treatment of 1 L of wastewater requires 0.95 kg of oxide overburden to achieve pH value of 2 and 99% of acid neutralization. Neutralization of acid prior to SX process is necessary since higher acidity can inhibit the process. Negative effect of impurities in solution, especially arsine formation and arsenic deposition during electrowinning process, will be avoided by applying solvent extraction followed by EW [9]. Expected efficiencies of the processes and copper recovery per 1 m^3 of wastewater are given in Table 7.

Table 7. *Expected efficiencies and copper recovery per 1 m^3 of wastewater*

	Characteristic	Unit	Value
Wastewater	Cu content	g/L	0.53
Overburden	Required amount	kg	957
PLS	Cu content	g/L	1.68
SX [2]	Efficiency	%	98
EW [2]	Efficiency	%	94
Entire process	Cu recovery	kg	1.55

Volume of residue, obtained in the simulation of acid neutralization/copper leaching process, is 7143.1 kg/h. The residue contains all the minerals from wastewater and oxide overburden that are insoluble in acid, Table 8, and it should be sent to solidification/stabilization (S/S) treatment.

Table 8. *Composition of acid neutralization/copper leaching residue*

Compound	wt%	Compound	wt%
Al_2O_3	18.89	Fe_2O_3	6.14
Cu	0.09	FeS_2	4.00
CuS	0.59	SiO_2	69.88

2.4 Zinc primary production by-products treatment

During the primary zinc production, leaching of zinc sulfide concentrate, jarosite group of minerals [19,20] and zinc neutral leach residue is obtained [21]. These by-products, zinc oxide jarosite – PbAg and zinc neutral leach residue, contain significant amounts of valuable metals (Ag, In, Ge), why high efficient recovery of these metals represent one of the major technological challenges.
Within a scope of zinc primary production by-products, research group has investigated possibility to valorize these materials using Waelz process. The simulation of Waelz process, using Software Package for Waelz process (SPW) was studied. SPW is mathematical model used for calculation of technological parameters of processing zinc bearing materials in Waelz process. Used material was zinc oxide jarosite – PbAg residue (Concentrate A) and zinc neutral leach residue (Concentrate B). Experiments have been performed in order to verify the results obtained by simulation.
SPW is used for calculation of technological parameters of processing zinc bearing materials in Waelz process. This is mathematical model which is used for determination of real parameter values and relations which is adopted in system of automatic process control. Distribution of elements from raw materials to products (dust and clinker) is made, based on historical data from real production. Besides, SPW is used for assessment of the influence of introducing new raw materials on techno-economic indicators.
Experiments have been performed after obtaining the model results. Defined quantity of Concentrate A (750 g) and Concentrate B (250 g) were measured and pelletized together with fine coke (<1 mm) and flux. Quantity of fine coke and flux was 20 % and 10 % of Concentrate A/Concentrate B mixture, respectively. The rest quantity of coke (> 1 mm), 260 g has been directly added to the furnace. Total quantity of coke was 46 % (460 g) of Concentrate A/Concentrate B mixture.
Experiments have been performed in short rotary furnace in order to optimize the temperature regime, furnace refractory lining and the amount of material. The furnace is equipped with a system for the collection of process gases and dust removal. The hood, which conducts emission gases to bag filter through a system of pipelines and coolers, was mounted above the furnace. Figure 1 shows technical design of short rotary furnace.

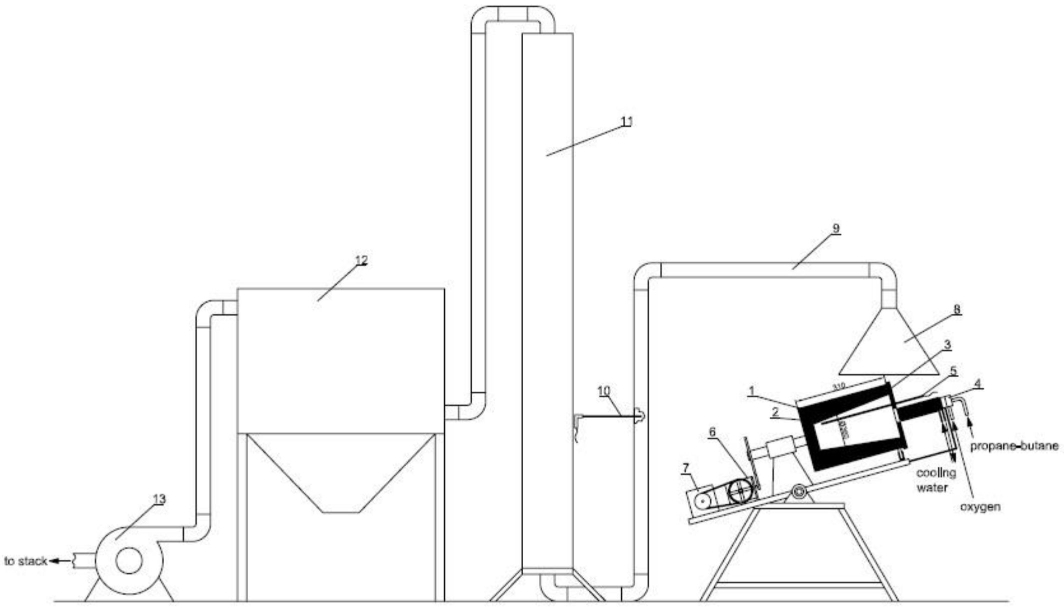

Figure 6. *Technical design of short rotary furnace: 1. Furnace refractory lining, 2. Furnace shell, 3. Cover, 4. Burner, 5. Thermocouple, 6. Reducer, 7. Electromotor, 8. Hood, 9. Off-gas pipeline, 10. Off- gas quality measuring, 11.Cooler, 12.Bag filter, 13. Fan*

Results of chemical analysis of Concentrates A and B, are presented in Table 9.

Table 9. *Chemical analysis of Concentrate A and Concentrate B*

Element	Zn	Pb	Fe	Ag	Cu	S	K	Na	Mg	Al	Ca
Concentrate A, %	7.40	6.43	25.5	0.02	0.48	9.00	0.37	0.07	0.08	1.47	0.74
Concentrate B, %	22.9	4.83	33.0	0.01	0.95	1.92	0.14	0.03	0.16	1.33	0.56

Transfer of elements from input charge to clinker, obtained from process simulation using SPW and after experimental analysis, is presented in Table 10.

Table 10. *Transfer of elements to clinker from input charge*

Element	Zn	Pb	Fe	Ag	Cu	S	K	Na	Mg	Al	Ca
SPW, %	5.94	7.42	92.3	49.1	92.3	31.3	92.3	91.7	93.0	92.4	93.1
Experiment, %	9.46	3.32	64.9	92.3	89.5	12.7	99.0	98.9	38.8	93.3	30.1

Presented concept may be applied in three components system involving Electric arc furnace dust (EAFD) as a source of zinc and lead. In addition, one part of coke may be substituted with various types of waste plastic, as an alternative fuel and reducing agent.

3. Conclusions

In order to secure a reliable and sustainable supply of TM, innovative solutions need to be developed along the entire value chain. This transition requires multi-stakeholder partnerships that foster innovation and entrepreneurship, which can be obtained by applying the Triple Helix concept. The relationships between the components of the helix concept, university-industry-government relationships, are of crucial importance for facing the challenges coming from high process complexity and multidisciplinary approach, and which individual helix components cannot resolve. Therefore, determination of clear programs focused on sustainable mining and material production methods, substitution of critical metals and recovery of metals from secondary sources should be major priority. Second relationship, begins at university level by giving societal challenges and sustainability concepts a central role throughout all curricula. The third relationship is the creation of an entrepreneurial and innovative mentality in all components of the helix. The entrepreneurial institutes (Innovation centers, Knowledge transfer centers, etc.) have a pro-active position in putting knowledge to use and in creation of new knowledge, and are in central position in successful implementation of helix concept.

Serbia has a long tradition in both, zinc and copper primary production, resulting in generation of huge amounts of various by-products which are nowadays classified as valuable secondary materials, rather than typical waste streams. Moreover, forthcoming and inevitable increase in so called urban waste streams (WEEE, catalysts), is highly notable in Serbia as well. Therefore, innovative solutions are needed along the entire value chain, and their successful implementation is important not just from point of environmental protection, but also from point of resource efficiency and sustainable use of natural resources.

In this paper, compilation of scientific, theoretical and experimental results is presented, promoting the innovative synergy of various metals and industrial activities in metallurgy, resulting in profitable transformation of by-products and waste materials into resources.

As presented, focusing on treatment of specific by-products from zinc and copper primary production, as well on specific waste streams like WEEE and waste automotive catalysts, research group is actively contribute in creation and transfer of new knowledge, contributing to the EU sustainability policy.

Metals industry is traditionally part of the solution, not part of the problem in the scope of economic sustainable development, so take a chance!

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