

# Report on characterization of primary and secondary materials (final)

D1.2



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PARTNER	APPROVER
CLC.	FRANCISCO SANCHEZ



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## ABBREVIATIONS AND ACRONYMS

XRF	X-ray Fluorescence
XRD	X-ray diffraction
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometer
ICP-MS	inductively coupled plasma – mass spectrometry
FAAS	Flame Atomic Absorption Spectroscopy
ру	Pyrite
sl	Sphalerite
ср	Chalcopyrite
сv	Covellite
gn	Galena
td	Tetrahedrite
eng	Enargite
сс	Chalcocite
bn	Bornite
arp	Arsenopyrite
CRM	Critical Raw Materials
SME	Small Medium Enterprise
RIR	Reference Intensity Ratio
ROM	Run Of Mine



## 1. PURPOSE

#### **1.1 EXECUTIVE SUMMARY**

The WP1 is the first part of the IntMet project with an objective to collect and characterize primary and secondary raw materials to be studied and tested. The **primary raw materials** include ores, concentrates and middlings and these were provided by mining partners i.e. (i) polymetallic ores and concentrates by SOMINCOR, CLC and BOR INST; (ii) complex or low-grade ores, concentrates and middlings by KGHM and BOR INST. The **secondary raw materials** include flotation tailings and metallurgical wastes that will be supplied by the mining partners.

This work package was divided into four tasks concerning the following objectives:

- definition, collection and characterization of primary raw materials,

 definition, collection and characterization of secondary raw materials such as flotation tailings and metallurgical wastes,

 – collection and characterization of materials and intermediate by-products or final products generated in the various technology developments,

- control and management of the package and delivery of primary and secondary raw materials samples to be provided for testing under WP2, 3, 4, 5 and 6.

Task 1.1 deals with "ores, concentrates and middlings samples collection and characterisation". It was assumed to select, collect and characterize primary and secondary raw materials samples, provided for laboratory and pilot plant test works by mining companies. The following materials are considered:

- polymetallic ores, concentrates and tailings: SOMINCOR, CLC, BOR INST
- complex or low-grade copper ores, concentrates, middlings: KGHM, BOR INST.

Physical, chemical, mineralogical and microscopic analysis, which were chosen to fully characterize investigated materials, allowed to review the existing geological information and flotation plants databases. It was suggested in the project proposal to use the following methods analyzing the chemistry of primary materials: chemical analysis of major and minor metals - carried out using various techniques including: XRF, ICP-OES, ICP-MS, fire-assay; XRD, optical microscopy, optical mineralogy, automated quantitative mineralogy, electron microprobe analysis (EMPA) and metallographic microscopy - used to determine ore texture and quantitatively evaluate particular minerals amount as well as to investigate mineral geochemistry and compositional maps.



Regarding secondary raw materials (flotation tailings and metallurgical wastes), the is to overcome limitations related to polymetallic low grade and complex ores to achieve high efficiency recovery of valuable metals (Cu, Zn, Pb, Ag) and critical raw materials (Co, In, Sb). Beside the enhanced ores flotation and hydrometallurgical processing of copper concentrates including atmospheric-, pressure- and bio-leaching, also the secondary materials like tailings and metallurgical wastes were tested for metals recovery and sulfur valorization.

Secondary raw materials were thoroughly characterized before further processing and metals recovery. The chemical, physical, mineralogical and microscopic analysis were done for a particular group of materials. The considered secondary raw materials mentioned in this report include pyrite tailings and pyrite concentrate, solid residues from atmospheric leaching, pressure leaching, and bioleaching, sulfuric acids generated in hydrometallurgical plant, and effluents from hydrometallurgical processing of copper ores.



## 2. ROM CHARACTERIZATION

## 2.1 CLC ORE

The contribution of CLC in defining and characterizing task was to collect polymetallic ore and performed required analysis of this material. The overview of deposit as well as view of the sample were presented in FIGURE 1.



FIGURE 1. THE OVERVIEW OF CLC DEPOSIT AND SAMPLE COLLECTION

Three different methodologies were used to evaluate the elemental composition of this material using inductively -coupled plasma spectrometer. Namely, in the ME-ICPORE method material was subjected to highly oxidizing conditions of HNO<sub>3</sub>, KClO<sub>3</sub> and HBr and then the solution was treated with aqua regia; in ME-ICP81x, material was fused with sodium peroxide at 700°C; in ME-ICP41 sample decomposition was achieved by digestion in an aqua regia. These methods were complementary, as for example ME-ICPORE was not able to analyze refractory metals while ME-ICP41 was not appropriate for mercury. Results of elemental analysis, prepared by CLC, in weight % were presented in TABLE 1(data with asterix were given in ppm).



Method	Cu	Fe	Са	Pb	Zn	As	Mn	Bi	Cd	Hg	Мо	S	Ag	Sb	Со
ME- ICPORE	0.989	39.5	0.59	2.42	3.35	0.444	0.046	0.029	0.006	79*	<0.001	47.6	57*	0.086	0.031
ME- ICP81x	0.98	40.9	0.58	2.37	2.97	0.45	0.04	_	_	_	-	48.9	-	_	0.036
ME- ICP41	8970*	26.2	0.57	>10000*	>10000	2960*	289*	214*	55.6*	66*	8*	>10	49.7 *	546*	301*
Method	AI	В	Ва	Be	Cr	Ga	к	La	Mg	Na	Ni	Р	Sc	Se	Sr
ME- ICPORE	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_
ME- ICP81x	0.14	_	_	_	-	_	-	_	_	-	-	_	-	_	_
ME- ICP41	0.01	10*	20*	<0.5*	3*	<10*	<0.01	<10*	0.01	0.02	29*	<10*	<1*	<10*	16*
Method	Th	Ti	TI	U	v	w	_	-	-	-	-	-	-	-	-
ME- ICPORE	_	_	_	_	_	_	_	_	_	-	_	_	-	_	_
ME- ICP81x	_	_	_	_	_	_	_	_	_	-	_	_	_	_	_
ME- ICP41	<20*	<0.01	60*	10*	3*	10*									

#### TABLE 1. ELEMENTAL COMPOSITION OF CLC ORE, [%]

\* – values in ppm

These results showed that precision of elements detection was very high. Some rarely analyzed elements were also placed in the table to show completeness of used techniques. The mineralogical examination combined with quantitative analysis showed that material was composed mainly of pyrite and primary sulfides, present in polymineral fragments associated with each other and pyrite, while minor sulfides were observed in lesser extent. The precised data were presented in TABLE 2.

#### TABLE 2. MINERALOGY OF CLC ORE, [%]

		MINERAL											
Sample	Pyrite	Sphalerite	Galena	Chalcocite	Chalcopyrite	Covellite	Bornite	Tetrahedrite	Enargite				
HPP<2mm	84.67	11.1	2.41	0	1	0.35	0	0.35	0.12				

Particular minerals were identified in samples using metallographic microscope. Images were presented in figure 2.





FIGURE 2. IMAGES OF METALLOGRAPHIC MICROSCOPE OF CLC ORE: A – BIG PARTICLE SIZE OF PYRITE (PY) WITH SUBHEDRAL-ANHEDRAL AND PRIMARY-SECONDARY SULPHIDES; B – PRIMARY SULPHIDE WITH PYRITE (PY), SPHALERITE (SL) AND CHALCOPYRITE (CP) IN
 A MINOR PRESENCE OF GALENA (GN); C – POLYMETALLIC PARTICLE WITH PYRITE (PY), TETRAHEDRITE (TD) AND CHALCOPYRITE (CP);
 D – POLYMINERALIC FRAGMENT OF PRIMARY MINERALIZATION COMPOSED OF GALENA (GN) AND SPHALERITE (SL), WITH
 CHALCOPYRITE RELICS/RESIDUES; E – DETAIL OF POLYMINERAL FRAGMENT COMPOSED OF PYRITE (PY) AND COVELLITE (CV); F – DETAIL
 OF FRAGMENT COMPOSED OF TETRAHEDRITE (TD) THAT HAS BEEN MASSIVELY REPLACED BY ENARGITE (ENG).

Summarizing, the CLC ore was composed mainly of pyrite and primary sulphides. Sulphides were associated with each other in polymineral grains and then with pyrite. The particle size was lower than 2mm. There were apparent signs of corrosion observed within samples.



## 2.2 KGHM ORE

KGHM ore was collected from "Lubin-Małomice" deposit, which is located in the north-west part of the Lower Silesian Voivodeship, Poland. It is a stratoidal type deposit with copper-bearing materials present in sandstone of rotliegend and thill part of Zechstein. It is a seam (layered) deposit, locally discontinuous.

KGHM "Lubin-Małomice" ore consists of sulfide minerals with the following coexisting metals: silver, lead, zinc, cobalt, molybdenum, nickel and vanadium. These are present as their own minerals or isomorphic additives to copper-bearing minerals. In case of lead its content within carbonate-shale ore can be higher than for copper. The average concentration of lead is 0.12%, it is located mainly in galena as well as in copper-containing minerals. An increased amount of zinc is rarely observed and actually ranges from 0.00 to 0.05 %. Zinc is mostly present as sphalerite. Cobalt is represented by cobaltite and smaltite. These minerals are present in form of grains, which can be found in bornite and chalcosine or separately in shales. Molybdenum is located as isomorphic additive in pyrite, chalcopyrite and bornite, sometimes can be found in its own minerals. Vanadium can be found in shales and carbonates that are not making their own minerals and its main concentrations are combined with organic matter. The elemental composition of KGHM low grade ore was presented in a TABLE 3.

Sample	Cu	Pb	Zn	As	Ni	v	Bi	Cd	Hg	Мо	Re	Ag	Sb	Со
KGHM	1.19	0.16	<0.05	0.11	0.004	0.0056	0.0008	0.0026	0.0002	0.011	0.00015	0.0057	0.0046	0.011

TABLE 3. ELEMENTAL COMPOSITION OF KGHM LOW GRADE ORE, [%]

The density of the material was separately determined for three fractions i.e. carbonate ore, shale ore and sandstone ore, resulting in 2.6 t/m<sup>3</sup>, 2.5 t/m<sup>3</sup> and 2.3 t/m<sup>3</sup>, respectively. It should be emphasized that the sandstone ore is dominating within the investigated area with a content ca. 58%, while for carbonate ore and shale ore this is about and 27% and 15.2%, respectively.

Qualitative and quantitative evaluation of minerals identified within the ore were presented in TABLE 4 and TABLE 5.

	TABLE 4. MINERALOGY OF KGHM LOW GRADE ORE												
		MINERAL											
Sample	Pyrite	Quartz	Sphalerite	Chalcocite	Chalcopyrite	Galena	Bornite	Enargite	Dolomite	Calcite	Shale		
KGHM	FeS <sub>2</sub>	SiO <sub>2</sub>	ZnS	Cu₂S	CuFeS <sub>2</sub>	PbS	$Cu_5Fe_2S_4$	Cu <sub>3</sub> AsS <sub>4</sub>	CaMg (CO <sub>3</sub> ) <sub>2</sub>	CaCO₃	KAlSiCaMgO		



The full mineralogical analysis performed by KGHM is composed of 60 minerals. Because of table transparency, only the 11 most common were presented. The presence of tetrahedrite, barite, sanidine, and alusite and rutile was found in much lower amount.

#### TABLE 5. MINERALOGY OF KGHM LOW GRADE ORE, [%]

	MINERAL										
Sample	Pyrite	Quartz	Sphalerite	Chalcocite	Chalcopyrite	Galena	Bornite	Enargite	Dolomite	Calcite	Shale
KGHM	0.46	34.21	0.27	0.26	0.85	0.73	0.61	0.08	36.25	7.00	15.26

Microscopic images of the investigated ore were presented in FIGURE 3.



FIGURE 3. IMAGES OF METALLOGRAPHIC MICROSCOPE OF KGHM LOW GRADE ORE, IN REFLECTED LIGHT: A – CHALCOPYRITE (YELLOW) IN A DOLOMITE; B – COMBINATION OF SPHALERITE (BLUISH) WITH CHALCOPYRITE (YELLOW) AND BORNITE (GREY); C – NATIVE SILVER (WHITE) WITH STROMEYERITE (GREY), JALPAITE (PINK-OLIVE) AND BORNITE (DARK LILAC); D – AGGLOMERATION OF HYPIDOMORPHIC CASTAINGITE (CREAMY) WITHIN EPIGENETIC VEINS.



## 2.3 SOMINCOR ORE

Elemental composition of Somincor ROM was presented in TABLE 6.

#### TABLE 6. ELEMENTAL COMPOSITION OF SOMINCOR POLYMETALLIC ORE, [%]

Method	Cu	Fe	Pb	Zn	As	Bi	Cd	Hg	Мо	Ni	Cr	v	Ag	Sb	Со
Somincor	0.64	-	1.517	6.59	0.347	0.005	0.016	-	0.002	0.002	0.002	0.005	0.006	0.052	0.021



## **3. CONCENTRATES CHARACTERIZATION**

### **3.1 CLC POLYMETALLIC CONCENTRATE**

Material labeled as Bulk PMS4 was a CLC polymetallic concentrate that was analyzed within this task (CLC). Material was produced in a batch mode from a CLC ore. The elemental analysis was done for this sample according to the previously suggested ME-ICPORE methodology (CLC). Data were presented inTABLE 7. The results were confirmed by IMNR studies.

Sample	Cu	Fe	Са	Pb	Zn	As	Mn	Bi	Cd	Hg	Мо	S	Ag	Sb	Со
CLC	1.8	37.9	0.2	3.6	5.8	0.1	0.036	0.025	0.004	101*	0.002	47	85*	<0.01	0.055

#### TABLE 7. ELEMENTAL COMPOSITION OF CLC POLYMETALLIC CONCENTRATE, [%]

\* – values in ppm

Density of CLC polymetallic concentrate evaluated by IMNR using pycnometric analysis was 4.6295 t/m<sup>3</sup>.

Qualitative analysis was performed using XRD method with XRD pattern presented in FIGURE 4, while list of detected minerals with their structures was presented in TABLE 8 – data were listed in two rows for analysis obtained from CLC and IMNR because of some discrepancies.





#### TABLE 8. XRD RESULTS OF CLC POLYMETALLIC CONCENTRATE

					MINER	AL			
Sample	Pyrite	Quartz	Sphalerite	Gypsum	Chalcopyrite	Galena	Anglesite	Bassanite	Macphersonite
CLC (CLC)	FeS <sub>2</sub>	SiO <sub>2</sub>	ZnS	Ca(SO <sub>4</sub> ) (H <sub>2</sub> O) <sub>2</sub>	CuFeS <sub>2</sub>	PbS	PbSO <sub>4</sub>	MoS <sub>2</sub>	Pb <sub>4</sub> (SO <sub>4</sub> )(CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>
Sample	Pyrite	Bornite	Sphalerite	Chalcocite	Chalcopyrite	Galena	Covellite	Enargite	Tetrahedrite
CLC (IMNR)	FeS <sub>2</sub>	Cu₅FeS₄	ZnS	Cu₂S	CuFeS <sub>2</sub>	PbS	CuS	Cu₃AsS₄	(Cu,Fe) <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>

Quantitative evaluation of identified minerals, obtained by CLC and IMNR – by means of RIR (Reference Intensity Ratio) method, was presented in TABLE 9.

#### TABLE 9. MINERALOGY OF CLC POLYMETALLIC CONCENTRATE, [%]

					MINER	AL			
Sample	Pyrite	Quartz	Sphalerite	Gypsum	Chalcopyrite	Galena	Anglesite	Bassanite	Macphersonite
CLC (CLC)	78	2	8	1	5	2	2	2	<1
Sample	Pyrite	Bornite	Sphalerite	Chalcocite	Chalcopyrite	Galena	Covellite	Enargite	Tetrahedrite
CLC (IMNR)	82.59	0	6.46	0.54	6.28	1.08	0.72	1.08	1.26

Microscopic study in reflected light of the analysed sample highlighted the following minerals (listed in order of frequency): pyrite – FeS<sub>2</sub>; sphalerite – ZnS; galena – PbS; chalcopyrite – CuFeS<sub>2</sub> and covellite CuS.

Sample examined in reflected light was mainly composed of pyrite as grains with dimensions from less than 1 micrometer up to hundreds of micrometers. Pyrite occurred mostly as individual crystals, but also was associated with other minerals present in the sample. Sphalerite and galena were present as associated, while chalcopyrite was observed as independent crystals or associated with the sphalerite and pyrite.





FIGURE 5. IMAGES OF METALLOGRAPHIC MICROSCOPE OF CLC POLYMETALLIC CONCENTRATE, IN REFLECTED LIGHT: A – WITH PYRITE (PY), SPHALERITE (SPH), CHALCOPYRITE (CPY) AND COVELLITE (CV) AND IN TRANSMITTED LIGHT: B – WITH PYRITE (PY), SPHALERITE (SPH), GALENA (GL), CHALCOPYRITE (CPY) AND COVELLITE (CV).

Comparatively, images obtained from metallographic microscope by CLC were presented in FIGURE 6.







FIGURE 6. IMAGES OF METALLOGRAPHIC MICROSCOPE OF CLC BULK CONCENTRATE PMS4: *A* – GENERAL APPERANCE OF THE SAMPLE CONSISTING MAINLY OF PYRITE (PY) ENHEDRAL-ANHEDRAL AND BOTH PRIMARY AND SECONDARY SULPHIDES; *B* – VARIOUS MONO-AND POLYMINERALIC GRAINS LOCATED WITHIN SPECIMEN IN THE FOLLOWING COMBINATIONS: PYRITE (PY)–CHALCOPYRITE (CP) – SPHALERITE (SL), PYRITE (PY)–TETRAHEDRITE (TD)–CHALCOPYRITE(CP), PYRITE (PY)–COVELLITE (CV), GALENA (GN), CHALCOPYRITE (CP), SPHALERITE (SL); *C* – MIXED FRAGMENTS COMPOSED OF CHALCOPYRITE (CP) PARTIALLY REPLACED BY BORNITE (BN) AND COVELLITE (CV); *D* – POLYMINERALIC FRAGMENTS IN FORM OF: PYRITE (PY)–CHALCOPYRITE (CP) AND PYRITE (PY)–GALENA (GN) –SPHALERITE (SL); *E* – MONOMINERAL FRAGMENTS OF COVELLITE (CV), GALENA (GN), TETRAHEDRITE (TD), CHALCOCITE (CC), ENARGITE (ENG) AND SPHALERITE (SL).

Results of grain size analysis performed by IMNR were presented in TABLE 10 and in FIGURE 7.

Size class, mm	m, %	Undersize, %	Oversize, %
d > 0.150	1.80	100.00	1.80
0.100 < d < 0.150	1.43	98.20	3.23
0.090 < d < 0.100	0.80	96.77	4.02
0.071 < d < 0.090	1.80	95.98	5.82
0.063 < d < 0.071	0.78	94.18	6.60
0.040 < d < 0.063	7.63	93.40	14.23
0.032 < d < 0.040	6.54	85.77	20.77
0.025 < d < 0.032	14.05	79,23	34.82
d < 0.025	65.18	65.18	100.00

#### TABLE 10. GRAIN SIZE DISTRIBUTION OF CLC POLYMETALLIC CONCENTRATE





FIGURE 7. PARTICLE SIZE DISTRIBUTION OF CLC POLYMETALLIC CONCENTRATE.

## **3.2 BOR POLYMETALLIC MATERIAL**

Polymetallic ore supplied by BOR INST was collected from the open pit of Bobija mines – West Serbia. The entire sample was ground to the size class of – 12.5 mm, homogenized by the cone-ring method and ball-milled to the size of 3.35 mm. As prepared material was used in further chemical and physical analysis.



FIGURE 8. THE OVERVIEW OF BOBIJA MINE AND SAMPLING METHOD THAT WAS USED.



#### TABLE 11. ELEMENTAL COMPOSITION OF BOR POLYMETALLIC MATERIAL, [%]

Sample	Cu	Fe	Ca	Pb	Zn	As	Mn	Bi	Cd	Hg	Мо	S	Ag	Sb	Со
BOR material	1.77	23.8	0.08	4.62	4.92	0.309	0.037	0.006	0.01	587*	0.007	31.9	120*	0.169	0.001

Results of elemental composition analyzed using unified ME-ICPORE methodology (CLC) were consistent with BOR INST analysis performed using combination of ICP-AES, FAAS (Flame Atomic Absorption Spectroscopy), XRF (X-ray Fluorescence), gravimetry, fire assay and carbon and sulfur analysis as well as with IMNR results obtained for this material. Analysis performed by BOR INST also allowed to estimate ppm of Mo, Ni, Se, Sn and Ti.

Additionally, starting material was drilled for mechanical investigation. This part was performed in a Laboratory for Mechanical Rocks at the Mining and Metallurgy Institute Bor (FIGURE 9). These experiments were performed according to the national standards, given in brackets:

- determination of the bulk density with pores and cavities (SRPS B.B7.113)
- determination of the uniaxial compressive strength (SRPS B.B7.126)
- determination of the moisture content (SRPS B.B7.111)
- determination of the bulk density without pores and cavities (SRPS B.B7.112)
- determination of the tensile strength by indirect method (SRPS B.B7.127)

Results were presented in TABLE 12.



FIGURE 9. MECHANICAL TESTS OF THE POLYMETALLIC ORE FROM BOR: A – DRILLING SAMPLE; B –PRESS ANALYSIS.



Sample	Moisture w [%]	Density γ <sub>z</sub> [g/cm3]	Specific mass γ <sub>s</sub> [g/cm3]	<b>Compressive strength</b> σ <sub>p</sub> , [MPa]	Tensile strength σ <sub>z</sub> [MPa]
1	0.55	4.670	4.778	68.37	10.80
2	0.51	4.761	4.792	89.24	6.00
3	0.53	4.752	4.770	60.65	7.45
Mean value	0.53	4.728	4.780	72.75	8.08

#### TABLE 12. MECHANICAL CHARACTERISTIC OF BOR POLYMETALLIC MATERIAL

Density presented by BOR INST was in accordance with IMNR results that obtained 4.547 t/m<sup>3</sup> using pycnometer method. On the contrary, the bulk density of ore of size -12.7mm was calculated to 2.531 t/m<sup>3</sup> while for class 3.35 mm it was 2.619 t/m<sup>3</sup>.

The qualitative analysis performed by BOR INST for this material was done using X-ray powder diffraction. The XRD pattern was presented in FIGURE 10 and analysis results in TABLE 13.



#### FIGURE 10. XRD PATTERN OF BOR POLYMETALLIC MATERIAL

					MINERAL				
Sample	Pyrite	Sphalerite	Galena, syn	alpha-SiO₂	Zeolite A, (K, Zn)	Hematite	Barite	Trechmannite	beta-S
BOR	FeS2	ZnS	PbS	SiO <sub>2</sub>	$Zn_5K_2Al_{12}$	$Fe_2O_3$	BaSO <sub>4</sub>	AgAsS <sub>2</sub>	S

#### TABLE 13. XRD RESULTS OF BOR POLYMETALLIC MATERIAL

With respect to these data, the XRD analysis performed at IMNR detected also cubanite, graphite, ramsbeckite and molybdenite.



The qualitative mineralogical analysis was performed using polarizing microscope for reflected and transmitted light brand "JENAPOL-U", company Carl Zeiss-Jena. The material was composed of pyrite, sphalerite, galena, tetrahedrite, chalcopyrite, covellite, arsenopyrite and gangue minerals, which were quartz, silicates and secondary minerals of Pb and Cu (anglesite, malachite, etc.). The content of barite was separated and obtained on the basis of chemical analysis. The quantitative mineralogical analysis allowed to evaluate the content of each mineralogical phase in the ore (TABLE 14). The surfaces of tested aggregates were determined using the software package OZARIA v2.5 and system for photomicrography. The RIR (Reference Intensity Ratio) method for minerals analysis, which was performed by the IMNR, showed also presence of cubanite, graphite, ramsbeckite and molybdenite in amount of 3.9 %, 2.4 %, 1.7 % and 0.3 %, respectively.

	TABLE 14. MINERALOGY OF BOR POLYMETALLIC MATERIAL, [%]											
					MINERAL							
Sample	Pyrite	Sphalerite	Galena	Chalcopyrite	Covellite	Arsenopyrite	Barite	Tetrahedrite	Waste			
BOR	45.15	7.71	7.57	0.04	0.04	<0.01	25.26	3.11	11.13			

Based on the mineral microscopic analysis it was showed that polymetallic Bobija deposit was comprised of the following minerals: sulphides (pyrite, sphalerite, wurtzite, galena, arsenopyrite, marcasite, pyrhotite, chalcopyrite, covellite, chalcocite), sulphosalts (tetrahedrite, tennantite), metals (native silver), non-metallic minerals (barite) and gangue minerals (quartz, chalcedony, carbonates).

Material examined in reflected light showed prevalence of pyrite in form of crystalline aggregates with a size between 1 and hundreds of micrometers. Other minerals usually occured inside the crystalline aggregates of pyrite, localized within cracks. Sphalerite and galena occured as independent grains or intercrystalline grains inside of pyrite grains forming domains with dimensions between microns and tens of microns. Covellite appeared as micron size granules, most often associated with sphalerite inside the pyrite granules or independently. Chalcocite and chalcopyrite occured most often as crystals with sizes below one micrometer up to micrometers, disseminated within crystalline aggregates of pyrite. Micronic crystals of tennantite-tetrahedrite were sometimes observed with chalcocite. Transmitted light of sample immersed in nitrobenzene revealed the abundant presence of barite as crystals with sizes between microns to tens microns.





FIGURE 11. IMAGES OF METALLOGRAPHIC MICROSCOPE OF BOR POLYMETALLIC ORE, IN REFLECTED LIGHT: *A* – WITH PYRITE (PY), SPHALERITE (SL), COVELLITE (CV), GALENA (GN), AND IN TRANSMITTED LIGHT: *B* – WITH BARITE (BRT) AND OPAQUE MINERALS (OP).

Grain size distribution was analyzed using laser particle size analyzer as well as a series of standard sieves (BOR INST). Results of sieving was presented in TABLE 15 and laser analysis schematically in FIGURE 12. Results obtained using both techniques were the same. The average particle diameter obtained by IMNR was as high as 41.82 microns.

Size class, mm	m, %	Undersize, %	Oversize, %
-0.500+0.425	1.20	100.00	1.20
-0.425+.0300	1.80	98.80	3.00
-0.300+0.212	2.20	97.00	5.20
-0.212+0.150	5.40	94.80	10.60
-0.150+0.106	8.40	89.40	19.00
-0.106+0.075	10.30	81.00	29.30
-0.075+0.053	5.30	70.70	34.60
-0.053+0.038	6.70	65.40	41.30
-0.038	58.70	58.70	100.00

#### TABLE 15. GRAIN SIZE DISTRIBUTION OF BOR POLYMETALLIC MATERIAL





## **3.3 KGHM POLYMETALLIC CONCENTRATE**

Elemental composition of KGHM material was determined using previously described ME-ICPORE methodology (CLC), additionally similar results were obtained by IMNR. Data were presented in TABLE 16.

Sample	Cu	Fe	Ca	Pb	Zn	As	Mn	Bi	Cd	Hg	Si	S	Ag	Sb	Со
KGHM	12,9	8.24	4	4.67	1.12	0.53	0.11	<0.005	0.006	<8*	6,5	13	642*	0.012	0.142

#### TABLE 16. ELEMENTAL COMPOSITION OF KGHM LOW GRADE CONCENTRATE, [%]

\* value in ppm

Density of the material was established by pycnometer method to level 2.8138 t/m<sup>3</sup> (IMNR).

Qualitative analysis of minerals using XRD method and semiquantitative using RIR method, performed at IMNR, were presented in FIGURE 13 and TABLE 17 and TABLE 18.





#### TABLE 17. XRD RESULTS OF KGHM LOW GRADE CONCENTRATE

		MINERAL												
Sample	Pyrite	Galena	Sphalerite	Chalcopyrite	Bornite	Dolomite	Rectorite	Biotite	Quartz					
KGHM	FeS <sub>2</sub>	PbS	ZnS	CuFeS <sub>2</sub>	Cu₅FeS₄	CaMg(CO <sub>3</sub> ) <sub>2</sub>	K <sub>1.2</sub> Al <sub>4</sub> Si <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub> ·4H <sub>2</sub> O	KFeMg <sub>2</sub> (Al Si <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	SiO <sub>2</sub>					

The semiquantitaive analysis obtained using RIR method resulted in content evaluation for identified minerals (TABLE 18) – IMNR.

#### TABLE 18. MINERALOGY OF KGHM LOW GRADE CONCENTRATE, [%]

	MINERAL												
Sample	nple Pyrite Galena Sphalerite		Chalcopyrite	Bornite	Dolomite	Rectorite	Quartz						
KGHM	10	5	2	7	19	19	9	5	14				

Microscopic study in reflected and transmitted light highlighted the following minerals (listed in order of frequency): chalcopyrite –  $CuFeS_2$ ; carbonaceous matter – C; quartz – $SiO_2$ ; bornite –  $Cu_5FeS_4$ ; rhombic chalcocite -  $Cu_2S$ ; pyrite –  $FeS_2$ ; carbonate (Ca,Mg)CO<sub>3</sub>; sphalerite – ZnS; cubic digenite -  $Cu_2S$ ; galenite – PbS and covellite.

Material examined in reflected light was mainly composed of chalcopyrite in form of granules with dimensions from less than 1 micrometer up to hundreds of micrometers. Chalcopyrite was associated with pyrite, bornite and digenite. Apart from its associations with chalcopyrite, bornite appeared independently or was associated with digenite. Chalcocite appeared as independent granules or was associated with digenite and bornite. Apart from the above combinations, digenite occured rarely in the form of independent granules. Sphalerite and galena were present as independent or associated granules. Sometimes, in the structure of sphalerite chalcopyrite appeared. Covellite, as seperated or associated with bornite, was rarely observed. Carbonaceous matter occured as aggregates, layered, with dimensions of the order of hundreds of microns. These aggregates included micronized sulphur granules. The microscopic study carried out in transmitted light on a sample immersed in nitrobenzene showed the presence of some quartz and carbonate granules, of tens of microns, most often associated with opaque minerals (sulphides).





FIGURE 14. IMAGES OF METALLOGRAPHIC MICROSCOPE OF KGHM LOW GRADE CONCENTRATE, IN REFLECTED LIGHT: A – WITH PYRITE,(PY), BORNITE (BN), COVELLITE (CV), CHALCOPYRITE (CPY) AND GALENA (GL), AND IN TRANSMITTED LIGHT: B – WITH CHALCOPYRITE (CPY), BORNITE (BN), PYRITE (PY), DIGENITE (DG), SPHALERITE (SPH) AND GALENA (GL).

Additionally, microscopic images obtained by CLC were comparatively presented in FIGURE 15.





FIGURE 15. IMAGES OF METALLOGRAPHIC MICROSCOPE OF KGHM LOW GRADE CONCENTRATE: A – HETEROGENOUS GRAIN SIZE WITH LOW PYRITE (PY) CONTENT, PRIMARY AND SECONDARY COPPER SULPHIDES PRESENT; B – FREE SPECIES OF GALENA (GN), CHALCOPYRITE (CP), COVELLITE (CV) AND ASSOCIATED SPECIES CHALCOPYRITE (CP)-BORNITE (BN); C – PRIMARY MINERALIZATION COMPOSED OF TETRAHEDRITE (TD) AND CHALCOPYRITE (CP); D – PRIMARY MINERALIZATION COMPOSED OF SPHALERITE (SL) AND CHALCOPYRITE (CP) WITH BORNITE INCLUSIONS (BN); E – PRIMARY MINERALIZATION COMPOSED OF PYRITE (PY), CHALCOPYRITE (CP) AND ARSENOPYRITE (ARP); F – CU PARTICLES: COVELLITE (CV) AND CHALCOPYRITE (CP).

Results of particle size distribution determination obtained for KGHM concentrate at IMNR were presented in TABLE 19 and laser analysis plot in FIGURE 16.



Size class, mm	m, %	Undersize, %	Oversize, %
d > 0.150	0.99	100.00	0.99
0.100 < d < 0.150	2.98	99.01	3.96
0.090 < d < 0.100	6.08	96.04	10.04
0.071 < d < 0.090	10.00	89.96	20.04
0.063 < d < 0.071	4.21	79.96	24.25
0.040 < d < 0.063	20.15	75.75	44.40
0.032 < d < 0.040	16.18	55.60	60.58
0.025 < d < 0.032	19.37	39.42	79.95
d < 0.025	20.05	20.05	100.00

#### TABLE 19. GRAIN SIZE DISTRIBUTION OF KGHM LOW GRADE CONCENTRATE



FIGURE 16. PARTICLE SIZE DISTRIBUTION OF KGHM LOW GRADE CONCENTRATE



## 3.4 SOMINCOR POLYMETALLIC CONCENTRATE

Elemental composition of Somincor material was determined using previously described ME-ICPORE methodology. Results, both obtained by CLC and IMNR were very similar, data were presented in TABLE 20.

TABLE 20. ELEMENTAL	COMPOSITION	OF SOMINCOR	POLYMETALLIC	CONCENTRATE [%]
TADLE 20. LELIVILITIAL	contri ostrion	or sommeon	I OLIMICIALLIC	

Sample	Cu	Fe	Са	Pb	Zn	As	Mn	Bi	Cd	Hg	Si	S	Ag	Sb	Со
SOMINCOR	5 20	20.0	0.025	1/1 0	0 10	0.28	0.011	0.015	0 022	0 0091	05	10.1	0.0267	0.14	0.011
concentrate	5.20	29.9	0.025	14.0	9.10	0.20	0.011	0.015	0.022	0.0081	0.5	40.4	0.0207	0.14	0.011

Density of this material was estimated at 4.7028 t/m<sup>3</sup> (IMNR).

Qualitative analysis was done by X-ray powder diffraction method (IMNR). The obtained XRD pattern was presented in FIGURE 17, while qualitative evaluation of possible structures in TABLE 21.



#### TABLE 21. XRD RESULTS OF SOMINCOR POLYMETALLIC CONCENTRATE

		MINERAL												
Sample	Pyrite	Galena	Sphalerite	Chalcopyrite	Covellite	Ramsbeckite	Biotite	Quartz						
SOMINCOR	FeS <sub>2</sub>	PbS	ZnS	CuFeS <sub>2</sub>	CuS	Cu <sub>15</sub> (OH) <sub>22</sub> (SO <sub>4</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>6</sub>	KFeMg <sub>2</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(O H) <sub>2</sub>	SiO <sub>2</sub>						



The semiquantitaive analysis obtained using RIR method resulted in content evaluation for identified minerals (TABLE 22) – IMNR.

	MINERAL											
Sample	Pyrite	Galena	Sphalerite	Chalcopyrite	Covellite	Ramsbeckite	e Biotite Qua 1.0 0	Quartz				
SOMINCOR	54	15.4	13.4	13	1.2	1.1	1.0	0.9				

#### TABLE 22. MINERALOGY OF SOMINCOR POLYMETALLIC CONCENTRATE, [%]

Microscopic study (IMNR and CLC) in reflected and transmitted light highlighted the following minerals (in order of frequency): pyrite –  $FeS_2$ ; chalcopyrite –  $CuFeS_2$ ; galena – PbS; sphalerite – ZnS; cubanite–  $CuFe_2S_3$  and undetermined transparent minerals (possibly quartz). Sample examined in reflected light was mainly composed of pyrite as grains with dimensions from less than 1 micrometer up to hundreds of micrometers. Pyrite graines similarly to other minerals, were of micrometer dimension – less than micrometer. The other minerals occured as independent or associated with pyrite. Pyrite grains with low anisotropy were highlighted, characteristic for arsenopyrite. The study carried out in transmitted light for material immersed in nitrobenzene showed the presence of transparent grains, micrometric – undermicrometric, microscopically indeterminable. Microscopic images were presented in FIGURE 18.



FIGURE 18. IMAGES OF METALLOGRAPHIC MICROSCOPE OF SOMINCOR POLYMETALLIC CONCENTRATE, IN REFLECTED LIGHT: *A* – WITH PYRITE (PY), SPHALERITE (SPH), GALENA (GL), CHALCOPYRITE (CPY) AND CUBANITE (CB), AND IN TRANSMITTED LIGHT: *B* – WITH PYRITE (PY), CHALCOPYRITE (CPY), GALENA (GL) AND SPHALERITE (SPH) WITH YELLOW-BROWN INTERNAL REFLECTIONS.



Mineralogical analysis was performed using metallographic microscope. Images obtained from the microscope were presented in FIGURE 19.



FIGURE 19. IMAGES OF METALLOGRAPHIC MICROSCOPE OF SOMINCOR SAMPLE: A – HETEROGENOUS GRAIN SIZE, PYRITE (PY) AS A MAIN SPECIES, HIGH LEVEL OF PRIMARY SULPHIDES ASSOCIATED TO PYRITE (PY); B – PYRITE (PY) DETAIL WITH PRIMARY SULPHIDES, SPHALERITE (SL), GALENA (GN) AND TETRAHEDRITE (TD); C – PYRITE (PY) PARTICLE WITH SPHALERITE (SL); D – PRIMARY SULPHIDE PARTICLE CONTAINING PYRITE (PY), GALENA (GN) AND CHALCOPYRITE (CP).

Results of grain size analysis performed by IMNR were presented in TABLE 23 and in FIGURE 20.



Size class, mm	m, %	Undersize, %	Oversize, %
d > 0.150	0.57	100.00	0.57
0.100 < d < 0.150	0.57	99.43	1.14
0.090 < d < 0.100	0.37	98.86	1.52
0.071 < d < 0.090	0.62	98.48	2.13
0.063 < d < 0.071	0.60	97.87	2.73
0.040 < d < 0.063	4.76	97.27	7,50
0.032 < d < 0.040	4.46	92.50	11.95
0.025 < d < 0.032	23.36	88,05	35.31
d < 0.025	64.69	64.69	100.00

#### TABLE 23. GRAIN SIZE DISTRIBUTION OF SOMINCOR POLYMETALLIC CONCENTRATE



FIGURE 20. PARTICLE SIZE DISTRIBUTION OF SOMINCOR POLYMETALLIC CONCENTRATE



## **3.5 BOR PYRITE CONCENTRATE**

The BOR pyrite concentrate was analyzed according to the similar methodology. At first elemental composition was determined using combination of ICP-AES, FAAS, XRF, gravimetry, fire assay and carbon and sulfur analysis. Results obtained by BOR INST and IMNR were similar and were presented in TABLE 24.

SAMPLE	Cu	Fe	CaO	Pb	Zn	As	Hg	S	Si	Ag	Al <sub>2</sub> O <sub>3</sub>	С
BOR pyrite	1.77	39.29	0.83	0.014	0.009	0.011	0.0001	44.04	4.11	0.0008	1.75	0.7
SAMPLE	MgO	Se	SiO2	Ti								
BOR pyrite	0.07	0.009	7.96	0.027								

TABLE 24. ELEMENTAL COMPOSITION OF BOR PYRITE CONCENTRATE, [%]

Additionally, Ba, Cd, Ga, La, Te and Zr were found at levels lower than 0.001 %, while Cr, Ge and V at levels lower than 0.005 %.

BOR pyrite concentrate density evaluated by IMNR using pycnometric analysis was 4.3225 t/m<sup>3</sup>.

Qualitative analysis performed at BOR INST using XRD method (FIGURE 21) revealed 4 structures i.e. pyrite (FeS<sub>2</sub>), quartz (SiO<sub>2</sub>), calcite (Ca(CO)<sub>3</sub>) and potassium in form of Cu<sub>8</sub>K<sub>3</sub>S<sub>6</sub>.



The same type of analysis prepared by IMNR demonstrated 14 different minerals, and 8 most common were presented in TABLE 25.



#### TABLE 25. XRD RESULTS OF BOR PYRITE CONCENTRATE

	MINERAL											
Sample	Pyrite	Quartz	Sphalerite	Gypsum	Chalcopyrite	Rutile	Covellite	Molybdenite				
BOR pyrite	FeS <sub>2</sub>	SiO <sub>2</sub>	ZnS	Ca(SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub>	CuFeS <sub>2</sub>	TiO <sub>2</sub>	CuS	MoS <sub>2</sub>				

The other possible structures include: hydronium jarosite  $- (K,H_3O)Fe_3(SO_4)_2(OH)_6$ , wroewolfeite  $- Cu_4(OH)_6(SO_4)(H_2O)_2$ , alunite  $- KAI_3(SO_4)_2(OH)_6$ , pyrophyllite  $- (AI_4Si_8O_{20}(OH)_4)_{.3333}$ , diaspore - AIOOH and biotite  $- KFeMg_2(AISi_3O_{10})(OH)_2$ .

Quantitative analysis of pyrite concentrate performed by IMNR was presented in TABLE 26. Content of sulfide mass in the whole sample was as high as 84.4%.

#### TABLE 26. MINERALOGY OF BOR PYRITE CONCENTRATE, [%]

		MINERAL												
Sample	Pyrite	Quartz	Wroewolfeite	Hydronium jarosite	Sphalerite	Gypsum	Chalcopyrite	Covellite	Alunite					
BOR pyrite	79.6	10.4	2.3	1.6	0.01	1.3	0.8	0.6	1.3					

Microscopic study (IMNR) in reflected light and in transmitted light of the analysed sample highlighted the following minerals (in order of frequency): pyrite –  $FeS_2$ ; sphalerite – ZnS; covellite – CuS; chalcopyrite – CuFeS<sub>2</sub>; bornite – Cu<sub>5</sub>FeS<sub>4</sub>; magnetite –  $Fe_3O_4$ ; carbonaceous material (coke, charcoal) and quartz – SiO<sub>2</sub>.

Sample examined in reflected light was mainly composed of pyrite in a form of grains with size between 1 micrometer to hundreds of micrometers. Other minerals were usually associated with pyrite. Sphalerite appeared as independent grains or was associated with pyrite and covellite. Covellite appeared as having dimensions from 1 micron up to hundreds of microns, most often associated with pyrite, or in the form of globular particles with dendritic structure. Covellite was present on the cracks into bornite granules or as bornite exclusions. Chalcopyrite was observed as grains with dimensions of up to hundreds of microns, independent or associated with pyrite. Bornite occured as crystals with under-micron dimension, with dendritic structure embedded into globular covellite. In addition, bornite was found as granules with dimension up to hundreds of microns, independent or associated with covellite. Magnetite was accidentally found in globular glass particles, perhaps fayalitic glass or as microcrystals in bornite. Carbonaceous matter was accidentally detected as charcoal and coke. The study carried out in transmitted light on a sample immersed in nitrobenzene showed the abundant presence of quartz as crystals with sizes from microns up to hundreds of microns.





FIGURE 22. IMAGES OF METALLOGRAPHIC MICROSCOPE OF BOR PYRITE CONCENTRATE, IN REFLECTED LIGHT: A – WITH PYRITE (PY), SPHALERITE (SPH), COVELLITE (CV), CHALCOPYRITE (CPY), AND IN TRANSMITTED LIGHT: B – WITH QUARTZ (QTZ).

Particle size distribution was determined using laser particle size analyzer as well as a series of standard sieves. Results of sieving was presented in TABLE 27 and laser analysis in FIGURE 23.

Size class, mm	m, %	Undersize, %	Oversize, %
-0.300+0.212	5.00	100.00	5.00
-0.212+0.150	2.50	95.00	7.50
-0.150+0.106	6.00	92.50	13.50
-0.106+0.075	16.00	86.50	29.50
-0.075+0.053	10.50	70.50	40.00
-0.053+0.038	11.50	60.00	51.50
-0.038	48.50	48.50	100.00

TABLE 27. GRAIN SIZE DISTRIBUTION OF BOR PIRYTE CONCENTRATE



These data were in accordance with results presented by IMNR.



## **3.6 CLC PYRITE TAILINGS**

Residual pyrite was characterized by IMNR. The elemental composition was obtained according to the methods presented above.

Sample	Cu	Fe	Са	Pb	Zn	As	Mn	Bi	Cd	Hg	Si	S	Ag	Sb	Со
CLC pyrite	0.75	38.20	0.70	1.7	1.4	0.36	0.021	0.012	0.012	-	2.09	51.58	-	0.048	-

#### TABLE 28. ELEMENTAL COMPOSITION OF CLC PYRITE CONCENTRATE, [%]

Density of this material was estimated at 4.6353 t/m<sup>3</sup> (IMNR).

Qualitative analysis was performed using XRD method with a pattern presented in **figure 24**, while list of detected minerals with their structures was presented in TABLE 29.



#### TABLE 29. XRD RESULTS OF CLC PYRITE CONCENTRATE

		MINERAL								
Sample	Pyrite	Quartz	Sphalerite	Gypsum	Chalcopyrite	Galena	Anglesite	Bassanite	Macphersonite	
CLC pyrite	FeS <sub>2</sub>	SiO <sub>2</sub>	ZnS	Ca(SO <sub>4</sub> ) $\cdot$ (H <sub>2</sub> O) <sub>2</sub>	CuFeS <sub>2</sub>	PbS	PbSO <sub>4</sub>	MoS <sub>2</sub>	Pb <sub>4</sub> (SO <sub>4</sub> )(CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	

Quantitative evaluation of identified minerals, obtained by IMNR – using RIR (Reference Intensity Ratio) method, was presented in TABLE 30.



#### TABLE 30. MINERALOGY OF CLC PYRITE CONCENTRATE, [%]

		MINERAL								
Sample	Pyrite	Quartz	Sphalerite	Gypsum	Chalcopyrite	Galena	Anglesite	Bassanite	Macphersonite	
CLC pyrite	78	2	8	1	5	2	2	2	<1	

Microscopic study in reflected light highlighted the following minerals (in order of frequency): pyrite –  $FeS_2$ ; sphalerite – ZnS; chalcopyrite – CuFeS<sub>2</sub>; galena – PbS; bornite – Cu<sub>5</sub>FeS<sub>4</sub>; chalcocite – Cu<sub>2</sub>S and covellite – CuS.

Sample examined in reflected light was composed mainly of pyrite as grains with dimensions from less than 1 micrometer up to hundreds of micrometers. Pyrite occured mostly as individual crystals, and associated with other minerals present in the sample. Sphalerite occurred as associated with pyrite, galena, chalcopyrite. Chalcopyrite occured individually as well as was associated with pyrite, bornite. Galena occured individually and associated with pyrite. Bornite was present as individual and associated with chalcocite and pyrite. Covellite was associated with pyrite.



FIGURE 25. IMAGES OF METALLOGRAPHIC MICROSCOPE OF CLC PYRITE TAILINGS, IN REFLECTED LIGHT: A - WITH PYRITE (PY), SPHALERITE (SPH), CHALCOCITE (CHC), BORNITE (BN) AND COVELLITE (CV), AND IN TRANSMITTED LIGHT: B - WITH PYRITE (PY), AND GALENA (GL).

Results of grain size analysis performed by IMNR were presented in TABLE 31 and in FIGURE 26.



Size class, mm	m, %	Undersize, %	Oversize, %
d > 0.150	2.32	100.00	2.32
0.100 < d < 0.150	4.22	97.68	6.55
0.090 < d < 0.100	3.55	93.45	10.09
0.071 < d < 0.090	6.12	89.91	16.21
0.063 < d < 0.071	3.21	83.79	19.42
0.040 < d < 0.063	18.59	80.58	38.01
0.032 < d < 0.040	13.67	61.99	51.68
0.025 < d < 0.032	10.13	48.32	61.82
d < 0.025	38.18	38.18	100.00

#### TABLE 31. GRAIN SIZE DISTRIBUTION OF CLC PYRITE TAILINGS



FIGURE 26. PARTICLE SIZE DISTRIBUTION OF CLC PYRITE TAILINGS.

#### **3.7 SOMINCOR PYRITE CONCENTRATE**

Material deliverd by Somincor was thoroughly analyzed at IMN with respect to elements composition, particle size distribution and qualitatively with respect to its content of minerals.



#### TABLE 32. ELEMENTAL COMPOSITION OF SOMINCOR PYRITE TAILINGS, [%]

Sample	Cu	Fe	Ca	Pb	Zn	As	Mn	Bi	Si	S	Ag	Sb	Со
Somincor pyrite	0.42	42.4	-	0.98	2.06	-	_	-	_	46.05	0.0045	0.049	0.012

Qualitative analysis was performed using XRD method, the resulting pattern was presented in FIGURE 27.



FIGURE 27. XRD PATTERN OF SOMINCOR PYRITE TAILINGS.

Material contained mostly pyrite –  $FeS_2$ , but also sfalerite – ZnS and quartz – SiO<sub>2</sub>. In very tiny amount basanite  $CaSO_4(H_2O)_{0.5}$  was present and probably in trace amount aluminosilicate of kaolinite structure  $Al_4(OH)_8Si_4O_{10}$  or minerals such as serafinite (Mg,Fe)<sub>6</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>. However, diffraction lines intensity from these minerals were too weak to define it perfectly.

Structural analysis using X-ray microanalyzer JXA 8230, JEOL was performed (IMN). Samples were sputtered with thin gold layer to avoid charge agglomeration. This produced a signal in recorded spectra due to  $M_{\alpha}$  Au line.



This technique allowed to prepare elements distribution and perform qualitative and quantitative point analysis using EDS mode. Maps of elements were presented in FIGURE 28.



FIGURE 28. ELEMENTS DISTRIBUTION WITHIN SELECTED AREA USING MAGNIFICATION 400X.

Qualitative and quantitative analyses were performed for selected points – presented in FIGURE 29.





Spectra for points 1, 2, 3 and 4, where points 1 and 4 were attributed to iron in form of FeS<sub>2</sub>.







FIGURE 29. QUANTITATIVE ANALYSIS USING EDS METHOD FOR PREVIOUSLY SELECTED POINTS.





Fig. 30. Particle size distribution of Somincor pyrite tailings.



## 4. SECONDARY RAW MATERIALS

### 4.1 PYRITE CONCENTRATE & TAILINGS FOR IRON RECOVERY AND SULFUR VALORIZATION

The pyrite tailings from Cobre Las Cruces and pyrite concentrate delivered by BOR were used to recover iron and valorize sulfur. The elemental composition of the starting materials was determined using combination of ICP-AES, FAAS, XRF, gravimetry, fire assay and carbon and sulfur analysis. Specific data were presented in TABLE 33and TABLE 34.

Sample	Cu	Fe	Ca	Pb	Zn	As	Mn	Bi	Cd	Si	S	Sb
CLC pyrite	0.75	38.20	0.70	1.7	1.4	0.36	0.021	0.012	0.012	2.09	51.58	0.048

#### TABLE 33. ELEMENTAL COMPOSITION OF CLC PYRITE CONCENTRATE, [%]

#### TABLE 34. ELEMENTAL COMPOSITION OF BOR PYRITE CONCENTRATE, [%]

SAMPLE	Cu	Fe	CaO	Pb	Zn	As	Hg	Si	S	Al <sub>2</sub> O <sub>3</sub>	С	Ti
BOR	1 77	30.20	0.83	0.014	0.009	0.011	0.0001	4 11	44.04	1 75	07	0.027
pyrite	1.//	57.27	0.85	0.014	0.009	0.011	0.0001	4.11	44.04	1.75	0.7	0.027

The qualitative analysis was performed by X-ray powder diffraction (FIGURE 30, FIGURE 31), the revealed structures together with the analyzed amount of particular minerals were presented in TABLE 35and TABLE 36.





FIGURE 30. XRD PATTERN OF CLC PYRITE CONCENTRATE







#### TABLE 35. XRD RESULTS OF CLC PYRITE CONCENTRATE

		MINERAL								
Sample	Pyrite	Quartz	Sphalerite	Gypsum	Chalcopyrite	Galena	Anglesite	Bassanite	Macphersonite	
CLC pyrite	FeS <sub>2</sub>	SiO <sub>2</sub>	ZnS	Ca(SO <sub>4</sub> )· (H <sub>2</sub> O) <sub>2</sub>	CuFeS <sub>2</sub>	PbS	PbSO <sub>4</sub>	MoS <sub>2</sub>	Pb4(SO4)(CO3)2 (OH)2	
%	78	2	8	1	5	2	2	2	<1	

#### TABLE 36. XRD RESULTS OF BOR PYRITE CONCENTRATE

		MINERAL								
Sample	Pyrite	Quartz	Sphalerite	Gypsum	Chalcopyrite	Rutile	Covellite	Molybdenite		
BOR pyrite	FeS <sub>2</sub>	SiO <sub>2</sub>	ZnS	Ca(SO <sub>4</sub> ) (H <sub>2</sub> O) <sub>2</sub>	CuFeS₂	TiO <sub>2</sub>	CuS	MoS <sub>2</sub>		
%	79.6	10.4	0.01	1.3	0.8		0.6			

Additionally, particle size distribution was determined using laser particle size analyzer as well as a series of standard sieves. Obtained data were presented in form of plots in FIGURE 32 and FIGURE 33.



FIGURE 32. PARTICLE SIZE DISTRIBUTION OF CLC PYRITE TAILINGS





FIGURE 33. PARTICLE SIZE DISTRIBUTION OF BOR PYRITE CONCENTRATE

These materials were subjected to oxidation in alkaline conditions (with potassium carbonate) at moderate temperature and pressure. To find the best conditions for pyrite oxidation the following parameters were analyzed: size of pyrite grains, temperature, air intake, total and partial pressure. The flowsheet of oxidation part was presented in FIGURE 34.



FIGURE 34. FLOWSHEET PRESENTING PTRITE OXIDATION

The solid part from pyrite oxidation was further processed to obtain commercial iron by-product. The iron oxide requirements that should be met in ferrous metallurgy are min. 55% Fe, and the following maximum concentration of other elements: 0.05% Cu, 9.02%Pb, 0.06% Zn, 0.13% As, 0.04% S, pellets should be of the specific size with 95% of diameter in the range 10-15mm, 5% under 10mm.



#### 4.2 PYRITE TAILINGS FOR PRE-CONCENTRATION

Flotation tailings delivered by Somincor, Portugal was used for pre-concentration and production of polymetallic concentrate, which can be recycled to hydrometallurgical cycle, and a rich pyrite concentrate. The results of grain and chemical analysis were presented in FIGURE 35 and TABLE 37.



Operator notes:

Malvern Instruments Ltd. Malvern, UK Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789 Mastersizer 2000 Ver. 5.60 Serial Number : MAL1021341 File name: Próby.mea Record Number: 2799 2016-08-02 08:01:49



Grain size analysis showed significant amount of fine particles in the provided material. About 70 % of the material being analyzed was composed of the finest class - 0.036mm. Cu, Zn, Pb and Fe content was investigated in an every grain class. A small variation of copper and zinc in a class +/-0.036mm was observed (Cu content in -0.036mm was 0.36% while in +0.036mm it was 0.51%, in case of zinc it was 1.41 % and 3.15%, respectively). The highest zinc content was observed in classes bigger than 0.075mm. Lead and iron content in + and - 0.036mm class was not significantly varied. Only + 0.2mm class showed an increased lead and decreased iron content.

Designation	Zinc (Zn)	Oxidized zinc (Zn(O))	Copper (Cu)	Oxidized copper (Cu(O))	Lead (Pb)	Oxidized lead (Pb(O))	lron (Fe)
Content [%]	2.06	0.702	0.42	0.07	0.98	0.27	42.4
Designation	Antimony (Sb)	Indium (In)	Cobalt (Co)	Silver (Ag)	Total sulfur (S <sub>t</sub> )	Sulfate sulfur (S <sub>s04</sub> )	Sulfide sulfur
Content [%]	0.049	<0.02	0.012	0.0045	46.05	0.98	45.07

#### TABLE 37. CHEMICAL OF SOMINCOR PYRITE TAILINGS

Chemical analysis was performed to estimate content of the following components: Cu, Pb, Zn, Fe, Ag, Co, In as well as total and sulfate sulfur ( $S_t$  and  $S_{SO4}$ , respectively), Cu(O), Pb(O) and Zn(O). Based on results obtained it was possible to evaluate oxidation degree of Cu, Pb and Zn: 16.7%; 27.6% and 34.6%, respectively and sulfide sulfur content – 45.07%.

X-ray diffraction was used to study crystalline phases of raw material (OP). Analysis was performed using X-ray diffractometer XRD7 Seifert-FPM with Co K $\alpha$  lamp and Fe filter in 2 $\Theta$  range from 10° to 100° that was assigned to interlayer distance d<sub>hkl</sub> from 1.027 to 0.1168 nm. Identification was based on database PDF-2 from 2007, ICDD company. Powders for analysis were appropriately prepared by mixing in ceramic mortar.

It was found that raw material - **OP** (FIGURE 36 contained mostly  $FeS_2$  and also sfalerite ZnS and quartz SiO<sub>2</sub>. In very tiny amount basanite  $CaSO_4(H_2O)_{0.5}$  was present and probably in trace amount aluminosilicate of kaolinite structure  $Al_4(OH)_8Si_4O_{10}$  or minerals such as serafinite (Mg,Fe)<sub>6</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>. However, diffraction lines intensity from these minerals were too weak to define it perfectly.





FIGURE 36. XRD PATTERN OF RAW MATERIAL - OP

Structural analysis with elements distribution within material was performed using X-ray microanalyzer JXA 8230, JEOL. Samples were sputtered with thin gold layer to avoid charge agglomeration. This produced a signal in recorded spectra due to  $M_{\alpha}$  Au line (FIGURE 37).

The following were performed:

- Images of secondary electrons (SEI) and backscattered electrons
- Elements distribution using energy dispersive x-ray spectroscopy (EDS)
- Qualitative and quantitative point analysis using EDS mode





FIGURE 37. XRD PATTERN AND ELEMENTAL COMPOSITION OF RAW MATERIAL - ANALYSIS IN TWO DIFFERENT POINTS

## 2.3 SOLID RESIDUE FROM HYDROMETALLURGICAL PROCESSING OF COPPER CONCENTRATE

## 2.3.1 SOLID RESIDUE FROM ATMOSPHERIC LEACHING

Atmospheric leaching conditions lead to dissolution of copper and zinc, leaving lead in the solid residue in the form of anglesite. Similar behavior is characteristic for silver and any precious metals present in the concentrate. The main goal of the task is to develop a method for efficient lead recovery in a form easy to smelt in conventional/low-cost rotary furnace process.

The copper concentrates delivered by Cobre Las Cruces, Somincor, BOR and KGHM were acid leached under atmospheric conditions. Processes were made with acid concentration 50g/L Fe<sup>3+</sup> addition at 90°C. Attempts were also made to use microwave assisted leaching in this case.

The pregnant leach solution was used for further metal winning, while solid residue was used to recover silver and lead. Tecnicas Reunidas, Spain, responsible for Pb&Ag recovery, received two types of atmospheric leaching residue samples for lead and silver recovery using a methanesulfonic acid. Methanesulphonic acid (MSA) leaching is an innovative technology to be applied for Pb and Ag recovery from atmospheric leaching residue. While maximum lead solubility in chloride media is not more than 0.15 M (>80 °C), MSA is a strong complex agent able to get high concentration of lead. The analysis of both starting material types were presented in TABLE 38.



ELEMENT	UNITS	RESIDUE 1W	RESIDUE 2W
HUMIDITY	%	29	12
DENSITY	g/cm <sup>3</sup>	3.6	4.3
COLOUR	-	GREY	GREY
Pb	%	6.27	4.12
Ag	ppm	1359	427
Zn	%	0.508	0.221
Cu	%	0.126	0.166
Fe	%	31.4	38.8
<b>SO</b> 4 <sup>2-</sup>	%	3.12	3.02
S <sup>0</sup>	%	16.6	5.79
ST	%	51.2	49.9

#### TABLE 38. SOLID RESIDUES FROM ATMOSPHERIC LEACHING

A third type (Residue 3) was supplied from CLC pilot plant in the mid-2017. Its analysis was presented in TABLE 39.

ELEMENT	UNITS	RESIDUE
Pb	%	6.69
Ag	ppm	972
Zn	%	0.258
Cu	%	0.395
Fe	%	34.4
As	%	0.39
Mn	ppm	250
Bi	ppm	410
Cd	ppm	<100
Hg	ppm	110
Мо	ppm	<100

#### TABLE 39. SOLID RESIDUE FROM ATMOSPHERIC LEACHING CLC PILOT PLANT



Со	ppm	140
<b>SO</b> 4 <sup>2-</sup>	%	4.62
S <sup>o</sup>	%	9.46
Sτ	%	49.3

Samples have been washed to remove the wetting liquor which contained high concentration of Fe and  $SO_4^{2^-}$ . Tests were performed to determine the influence of residence time, redox potential, temperature, solid/liquid ratio, calcium content in leachant and type of residue.

### 2.3.2 SOLID RESIDUE FROM PRESSURE LEACHING

As most of materials were reached at a later stage of the project, IMN has started a research producing its own pressure leaching residues that can be used for lead recovery. Pressure leaching, performed at IMN, was carried out in a reactor made of Hasteloy B2 with volume ca. 2 L, equipped with glass stirrer and heated by external mounted heating mantle. Based on past experience of IMN in such processes and regarding safety procedure the reaction was carried out at pressure 20 bars (7.5 bars O<sub>2</sub> overpressure) and temperature 190 °C (+/- 5 °C). Experiments were based on the KGHM copper concentrate. More than 50 trials were conducted to produce enough amount of material for further research. Process parameters were varied and generally three types of materials were obtained. Samples were prepared at different temperature and/or pressure as well as the various amount of oxidizing agent, as was shown below:

- tests at 190 °C and 20 bars (in further part of document denoted as 190C),
- tests at 140 °C and 20 bars (in further part of document denoted as 140C),
- tests at various temperature & pressure & oxidizing agent amount

Materials were analyzed qualitatively and quantitatively. Semiquantitative analysis using XRF method was performed to have an overview of elements present within samples. Then precise quantitative analysis of selected elements was performed. As elements of great influence Pb, Cu, Fe, As, Ag, Al and Si as well as S<sub>total</sub> and S<sub>SO4</sub> were selected. Results of semiquantitative analysis were presented in **table 8**.

Element	190C	140C	MiX
Al	4.05	4.09	4.00
Si	10.32	9.03	10.31
Fe	8.53	7.41	8.47
Cu	0.47	2.62	2.22
As	0.16	0.28	0.19
Ag	0.076	0.070	0.074
Pb	5.42	5.69	5.92
Stotal	8.30	14.3	10.04
S <sub>sulfate</sub>	7.45	6.30	6.51

TABLE 40. QUANTITATIVE ANALYSIS OF PRESSURE LEACHING RESIDUE FROM KGHM COPPER CONCENTRATE

Further, XRD analysis was performed to determine exact lead structure. Detected patterns for other metals were limited to have clear XRD signal of lead compound (because number of possible metal structures was too big – more than 15 metals present in samples). The XRD patterns registered for considered materials were presented in a FIGURE 38.



FIGURE 38. XRD PATTERNS OF PRESSURE LEACHING RESIDUES (REGISTERED FOR ALL THREE TYPES OF MATERIALS)

XRD analysis showed that lead was present in all three samples in form of lead jarosite (plumbojarosite) of a formula **PbFe**<sub>6</sub>(**SO**<sub>4</sub>)<sub>4</sub>(**OH**)<sub>12</sub>. This raised issue linked with proper Pb leaching as TETA solution is extremely selective for PbSO<sub>4</sub>. Consequently, in further research attempts have been made to decompose lead jarosite into more favorable anglesite form. Satisfied conversion of lead jarosite into lead sulfate allowed to use this leaching residue in a next stage to recover Pb.

The real project secondary raw materials in form of pressure leaching residues were delivered to IMN later. These materials were prepared from different concentrates (KGHM, Somincor, CLC and BOR) therefore the lead content



varied from about 10 to 29%. The concentration of other elements were as follows: 21-29% Fe, 0.02-0.035% Ag, 0.1-0.4% Cu and about 0.3% As. It was found that lead was partially present in form of anglesite and partially as jarosite. Distribution of lead between anglesite and jarosite for different pressure leaching residues from Outotec were presented in TABLE 41.

Pb-bearing material	OT8	ОТ9	OT10	OT11	OT12	OT13	OT14
Pb-jarosite	major	major	major	major	major	major	major
PbSO₄	lesser amount	absent	lesser amount	absent	absent	absent	absent

#### TABLE 41. PRESENCE OF LEAD IN PB-BEARING COMPOUNDS, BASED ON XRD ANALYSIS

Structural analysis of the starting materials from Outotec revealed presence of lead in form of both sulfate and jarosite form – **Fig. 10**. This enforced to convert Pb-jarosite to enhance lead recovery from these materials.



FIG. 10. XRD EXAMPLE FOR PRESSURE LEACHING RESIDUES FROM OUTOTEC

Generally, lead recovery from pressure leaching residue is a multistage process that was schematically presented in FIGURE 39.





#### FIGURE 39. SCHEMATIC BLOCK DIAGRAM OF LEAD RECOVERY USING AMINE SOLUTION

#### 2.3.3 SOLID RESIDUE FROM BIOLEACHING

Bioleaching tests of specific copper concentrates from the mining companies (Somincor, KGHM, CLC and Bor) were performed in a small laboratory-scale. Moderate thermophile cultures adapted to growing in the presence of very high base metal, lead, silver, and sulfates concentration were used in the program. This allowed to produce leached solution and solid residue for lab-scale metal extraction studies.

Lead, silver and gold were recovered from a bioleach residue using physical separation techniques. In the next part, the pilot plant arrangements will be constructed to verify results obtained in small-scale. The elemental analysis of bioleach residue delivered by Mintek was presented in TABLE 42.



Element	Pb	Zn	Cu	Fe	As	Sb	Ag	Hg	Cd
%	6.37	1.84	0.23	21.67	0.19	0.19	0.0133	0.07	0.00364

TABLE 42. CHEMICAL ANALYSIS OF POLYMETALLIC BIOLEACHING RESIDUE

Qualitative mineralogical analysis was carried out under a polarizing microscope for reflected light in the air, with identification of ore and non-ore minerals. Quantitative mineralogical analysis was carried out using the method of parallel sections, with distance of 1 mm. Measurements of tested grains were determined using the software package OZARIA v2.5 and the system for photomicrography. Results were presented in **table 11**.

Mineral	%				
Pyrite	53.51				
Sphalerite	3.75				
Galenite	<0.01				
Tetrahedrite	1.05				
Arsenopyrite	<0.01				
Covellite	<0.01				
Chalcopyrite	<0.01				
Anglesite	7.76				
Barite	22.71				
Waste	11.22				

TABLE 43. QUANTITATIVE MINERALOGICAL ANALYSIS OF BIOLEACHING RESIDUE

Pyrite is the most common sulfide mineral. All mineral grains with pyrite along the edges are intensively corroded. The main zinc mineral in a sample is sphalerite. According to its optical properties it corresponds to a variety with poor iron - kleophane. All mineral grains with sphalerite along the edges are intensively corroded. A smaller presence of tetrahedrite was found from copper minerals, while the presence of other Cu-minerals was not found. Gold minerals are not noticed. Most of the silver and mercury are structurally related to tetrahedrite. Waste are: barite, quartz and silicates.

Recovery of lead (leaching with sodium chloride), barium (firing with anthracite; melting with sodium carbonate and dissolution in hydrochloric acid), gold and silver (thiosulfate and ethylenediamine), was analyzed.

## 2.4 GYPSUM CRYSTALLIZATION FROM SPENT SULFURIC ACIDS

The objective of the task was focused on sulphuric acids generated in production process. Currently, these acids are neutralized with milk of lime, and the formed residue is deposited. The resulting residue can contain more than



80% of CaSO<sub>4</sub>•2H<sub>2</sub>O. One of the rational ways of management of such a waste can be seen in its processing into coarsely crystalline, easily dehydrating gypsum. Then gypsum can be used as a clinker additive for control of the rate of cement binding in the amount up to 5%. The production of gypsum from spent sulphuric acids and neutralization residues was based on crystallization of calcium sulphate from spent acids by neutralization with calcium carbonate.

In the preliminary part to this task coarse grain gypsum production using four selected spent weak sulfuric acids obtained from technological gases purification in copper and zinc industry (Sulphuric Acid Plants) were used. The chemical composition of these acids were showed in TABLE 44.

	Unit	Acid 1	Acid 2	Acid 3	Acid 4
рН		2.6	1.6	0.8	0.8
Mineral acidity	mEq/dm <sup>3</sup>	370	130	810	820
Cľ	mg/dm <sup>3</sup>	5200	250	1460	10600
<b>SO</b> <sub>3</sub> <sup>2-</sup>	mg/dm3	230	5700	2002	2740
<b>SO</b> <sub>4</sub> <sup>2-</sup>	mg/dm <sup>3</sup>	7330	3000	40190	28020
F	mg/dm <sup>3</sup>	3270	37.6	30	1488
Fe	mg/dm <sup>3</sup>	60.31	0.32	0.27	0.12
Zn	mg/dm <sup>3</sup>	48.1	135.6	59.4	0.14
Cd	mg/dm <sup>3</sup>	84	3.4	<0.1	<0.1
Pb	mg/dm <sup>3</sup>	13.4	7.6	4	0.16
As	mg/dm <sup>3</sup>	28.9	3.3	73	195.7
Cu	mg/dm <sup>3</sup>	no	5.8	4.2	<0.1
Ni	mg/dm <sup>3</sup>	no	<0.1	0.62	<0.1
TI	mg/dm <sup>3</sup>	65.9	4.2	no	no

TABLE 44. CHEMICAL COMPOSITION OF WASH ACIDS

The scope of the research included:

- gypsum crystallization experiments; initial parameters were selected based on partners' experience in coarse crystalline gypsum production,
- effect of pH evaluation on heavy metals content in produced gypsum, in the range 1.5 4,



 effect of temperature evaluation during gypsum neutralization and crystallization on quality of obtained crystals at 20°C, 50°C and 70°C.

In the latter part coarse crystalline gypsum production from waste acid supplied by First Qantum Minerals Ltd was investigated. The chemical composition of the supplied acid was presented in TABLE 45.

Value	H <sub>2</sub> SO <sub>4</sub> (g/L)	Cu (g/L)	Fe <sup>⊤</sup> (g/L)	Fe <sup>2+</sup> (g/L)	Cl (mg/L)	Ca (g/L)	Co (mg/L)	Mn (mg/L)	Pb (mg/L)	Zn (mg/L)	SO₄⁼ (g/L)	suspension (mg/L)
average	15.9	0.6	13.2	7.4	1420	0.69	172.83	92	6.3	1259	52.3	
max	24.0	1.5	18.9	9.4	1683	0.88	254	129	9.8	1690	67.1	
min	9.9	0.1	6.1	5.2	1107	0.54	78.4	40	3.4	573	26.4	
IMN	46.5	1.6	18.6		1550	0.71	130	93	4.6	1600	66.8	135

### TABLE 45. CHEMICAL ANALYSIS OF FQM ACID (BY SUPPLIER AND IMN)

Similarly to the previously prepared materials, the microscopic analysis of the produced crystals as well as moisture content in a standard vacuum filtration test (using Büchner funnel with 70mm diameter) were used as gypsum quality criteria.

## **2.5 WATERS AND EFFLUENTS PURIFICATION**

The aim of this task was focused on characterisation, purification, recycling and reuse of effluents produced by means of the mining activity. Recycling of valuable components, such as copper or antimony could result in very important metals recovery from waste effluents. Low pH values and high levels of metals and sulphates are expected in all major mining effluents. Some techniques proposed to purify these effluents include:

- Alkaline precipitation, coagulation and flocculation
- Selective recovery of metals using fractional treatments
- Removal of metals employing specific reagent or components (quelants, sorbents...)
- Ion exchange resin to recover valuable metals
- Membrane technologies to purify and remove some specific contaminants.

Considered samples were, effluents (secondary raffinate) from copper extraction process delivered by CLC, and wash liquor from zinc industry after gypsum crystallization sent by IMN. Quantitative analysis (**table 14**) was performed to present metal content that can be recovered from the tested solutions.



Parameter		ZGH – IMN sample	Secondary Raffinate- CLC	Secondary Raffinate- CLC	Secondary Raffinate- CLC	Secondary Raffinate- CLC	Secondary Raffinate- CLC
рН		1.96	1.09	1.02	0.94	0.91	0.90
Electrical conductivity	(mS/cm)	6.41	83.05	87.78	84.04	62.35	65.50
Al	mg/L	1.97	115.33	125.85	133.50	95.80	125.69
As	mg/L	14.06	688.00	802.48	902.92	649.86	807.61
Ba	mg/L	0.02	0.11	0.11	0.10	0.17	0.18
Ca	mg/L	746.11	521.90	351.39	437.55	542.52	604.58
Cd	mg/L	4.25	5.09	5.70	4.37	3.26	4.52
Со	mg/L	0.07	131.72	203.66	193.42	71.67	156.08
Cr	mg/L	12.12	6.74	7.37	6.86	4.81	6.65
Cu	mg/L	1.75	364.80	401.38	437.55	224.53	210.45
Fe	mg/L	41.71	13061.55	13282.56	13038.47	8744.72	10605.94
Mn	mg/L	1.62	77.53	89.62	85.47	56.43	75.39
Na	mg/L	0.01	1239.73	1242.09	1198.12	679.86	970.50
Ni	mg/L	23.73	7.02	8.72	7.85	4.07	7.61
Pb	mg/L	2.57	6.05	7.34	6.69	4.77	7.83
S	mg/L	837.00	17900.00	17789.00	17490.00	10957.00	13661.07
Sb	mg/L	0.02	38.31	44.61	45.06	46.30	49.16
Sn	mg/L	0.05	7.60	8.80	6.69	4.75	8.21
Ti	mg/L	0.41	2.19	2.51	2.10	2.09	4.13
V	mg/L	0.04	1.70	1.60	1.55	1.65	2.00
Zn	mg/L	127.46	840.13	1081.94	1063.13	850.03	1086.68

#### TABLE 46. QUANTITATIVE ANALYSIS OF EFFLUENTS

IMN sample presented low content on the most of the parameter and the others from CLC had high concentration of Fe, Cu, As and Zn. Based on the results obtained from AGQ previous studies, two technologies were those that showed the best results in terms of recovery /elimination of valuable metals from the effluent - these are: ion exchange and fractional/selective precipitation. Procedure of fractional precipitation technology was presented in FIGURE 40.





FIGURE 40. SCHEMATIC DIAGRAM OF FRACTIONAL PRECIPITATION TESTS

Ion exchange is also one of the most frequently applied processes for removal of heavy metals from wastewaters and mining effluents. This treatment is based on the ion-interchange between the solid phase (resin) and liquid phase (effluent). In this way, resin takes out ions from the liquid and discharges other ions of the same charge in an equivalent amount. Valuable metal can be recovered in a concentrated form by the elution of the resin with an appropriate agent. The application of the ion exchange procedure was tested using sample 1 (IMN) and 2 (CLC), because of varied metals content.



## 5. CONCLUSIONS

Witin the scope of the study **materials delivered by CLC, KGHM, BOR and Somincor** were characterized. These included polymetallic ores and concentrates and complex or low grade copper ores and concentrates and pyrite concentrates.

The complete elemental analysis was done for every material according to the best available methodology (ME-ICPORE). Additionaly, some samples were treated by different techniques like XRF, FAAS, carbon and sulphur analysis and gravimetry to entirely show the composition of the materials.

Real density of materials was determined using pycnometer method. In several cases also bulk density was determined.

XRD method was used for qualitative analysis of all materials. Except XRD patterns the obtained results were collected in tables showing the determined structure of the mineral.

Microscopis analysis with additional equipment setups was used to supplement XRD results i.e. the qualitative results as well as to perform quantitative evaluation of the particular minerals within each sample. This allowed to establish association between minerals within analyzed materials.

Particle size distribution was determined for every material either using laser particle analyzer or by set of sieves, or using both these methods.

Although similar level of copper can be found in CLC ROM (~1%) and KGHM ROM (~1.2%) the amount of other metals is varied. Lead content in CLC material is ca. 15 time higher (2.4% instead of 0.16% for KGHM), zinc content is 3.35% and lower than 0.05% for CLC and KGHM, respectively. Almost 20 times higher antimony content can be observed in CLC material and only 3 times bigger value of cobalt. In both materials the same silver amount was observed i.e. 0.0057%.

All concentrates, i.e. the polymetallic from CLC, Somincor and BOR as well as low grade from KGHM, were thoroughly analyzed to determine their elemental composition. Mostly, 15 elements were analyzed, which was sufficient for further research. In one case analysis covered more than 30 elements to show the precision of assumed methodologies. X-ray powder diffraction with microscopic techniques allowed to evaluate differences between materials with respect to their mineralogy. BOR and CLC have very similar Cu content (~1.8%), tripled



value was obtained for Somincor (5.2%), while the highest (13%) for material from KGHM. The highest Fe content was found in CLC (38%), also in Somincor (29%) and BOR concentrate (23%) these value were high. On the contrary KGHM concentrate has about 8% Fe. Zn and Pb content were as follows: 5.8% and 3.6%; 4.6% and 4.6%; 9.1% and 14.8%; 1.1% and 4.6%, respectively for CLC, BOR, Somincor and KGHM. The highest Ag content was found in KGHM material circa 640 ppm and only 85 ppm in the CLC one.

CLC material was mainly composed of pyrite (80%) with some sphalerite and chalcopyrite. BOR consisted of 45% pyrite, 25% barite and also sphalerite, galena and waste (11%). Somincor cointained 54% pyrite and almost equal (~15%) galena, sphalerite and chalcopyrite. Analysis of KGHM material showed 10% pyrite, ~20% bornite, ~20% dolomite, 9% rectorite and 14% quartz.

Additionally, BOR pyrite concentrate was taken into consideration in this report.

Within the scope of this study the **secondary raw materials** produced in the Intmet project were characterized. These included pyrite tailings and concentrates, solid residues from metals extraction, and effluents from hydrometallurgical processing.

The pyrite tailings for sulfur valorization and iron recovery, delivered from Spain (CLC) and Serbia (BOR) were quantitatively analyzed. The similar iron content i.e. 38.2% and 39.3% was found, respectively. Much bigger lead concentration (about two orders of magnitude) and arsenic (about one order) was found in CLC material. Additionally, presence of cadmium was observed. Qualitative analysis showed that except pyrite there were sphalerite and chalcopyrite mainly present in CLC tailings, while in BOR tailings quartz was found as a mineral in a bigger extent.

Flotation tailings delivered by Somincor were used to pre-concentration and production of polymetallic concentrate. Material was featured by the following metals content: iron – 42%, copper – ca. 0.4%, zinc ca. 2% and lead 0.95%. Additionally chemical analysis revealed the presence of antimony – 0.049%, cobalt – 0.012% and silver - 4.5ppm. Because of fine grains (about 70% below 0.036mm) it was really difficult to beneficiate it using flotation and gravitational methods. Sphalerite galena and chalcopyrite were identified as minerals of metals of interest. Quartz with some amount of kaolinite and chlorite group minerals were base of gangue. Among valuable minerals particularly galena existed in form of small grains below 1 Imm.

Solid residue from atmospheric leaching contained from 4 to about 7 % lead, 30-40% iron and 430 to 1360ppm of silver, and lead was present entirely as lead sulfate. In pressure leaching solid residues the lead was partially in form of jarosite and partially as lead sulfate. This was suggested as a crucial point as most of lead leachates allow to recover metal present as lead sulfate. Consequently, pressure leaching residues have to be transformed chemically to sulfates. Lead content in the materials varied from about 10 to 29%, while the concentration of other important elements was: 21-29% Fe, 0.02-0.035% Ag, 0.1-0.4% Cu and about 0.3% As. The bioleaching solid residue contained



6.4% lead, in form of anglesite. The highest concentration was found for pyrite (53.5%), barite (22.7%), anglesite (7.8%) and sphalerite (3.75%).

Spent weak sulfuric acids obtained from technological gases purification in copper and zinc industry (Sulphuric Acid Plants) were used for gypsum crystallization. Preliminary study applied material from Polish zinc and copper smelters. These effluents were characterized by varied concentration of chlorides, sulfites, sulfates, and fluorides, and were used to establish proper parameters of crystallization (pH, temperature, time etc.). In the latter part a waste acid supplied by First Quantum Minerals was used to obtained pure gypsum. The starting material was analyzed with respect to the metals content – presence of Pb, Mn, Zn, Co, Fe, and Cu was detected.

Different types of secondary raffinates from CLC were used to effluents purification tests. Different approaches (fractional precipitation and ion exchange) were used to recover metals from these solutions. Recovery of iron, copper, zinc and manganese were most important as concentration of these metals was significantly higher than others.