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Application of modern research methods for the evaluation of copper ores enrichment: new technologies

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ABSTRACT: In this paper the possibilities, as well the results, of application of certain modern methods of researches were presented. Among them, the scanning electron microscopy and X-ray diffractional analysis were applied to estimate the results of the newly introduced chemical-flotation technology of carbonate copper ores industrial enrichment in KGHM "Polska Miedź " S.A. in Lubin. The conducted research allowed the investigation of the feed, product modified by sulphuric acid and enrichment products of such chemically changed material. The obtained results were shown in pictures, scan maps and diffraction patterns. They contain the information of mineralogical composition of studied materials, elemental composition and samples' surface morphology. Thanks to the information obtained it is possible to choose the correct method of ore preparation and the method of enrichment with estimated its efficiency.

1 INTRODUCTION

A significant development of mineralogy as a science has been observed for a couple of years due to the implementation of new, modern research methods. Among them the scanning electron microscopy and X-ray diffraction analysis should be mentioned first. These techniques can be applied practically in every field as material science is concerned. There are many reports in which they were used, for example in the studies in metallurgy, fracture mechanics, in structural examination of metals and alloys, in the studies of surface phenomena (Sokolowski et al., 1980), investigations of defects in semiconductors and dielectric materials, as well as in observations of cathode luminescence effect in diamonds. SEM and XRD appeared very useful in palaeontology, in comparative studies of fossil crusts and actually occurring organisms.

Therefore both SEM and XRD have been applied in the studies related to the mineral raw material processing. The results thus produced are a source of information dealing with the assessment of efficiency of enrichment operation as well as the control of technological process.

In one report (Bigosiński and Drzymała, 1996) about "quantitative determination of chalcocite in the mixtures with galena after surface thermal treatment" the X-ray diffraction was used to identify the sulphides. The samples were observed under the microscope after heating. The population of red particles (chalcocite after thermal treatment) was countered following the planimetric method under the microscope.

In another work concerning the "use of bacterial leaching in the incineration wastes processing" the SEM pictures illustrated well the morphology of samples before and after lixiviation; simultaneously, the microprobe analysis contributed to the identification of particular grains (Fecko et al., 1996).

The determination of optical-geometrical parameters, based on the image analysis linked with energy dispersive microanalysis by X-rays, phase analysis and other methods were adapted in the other project, for the assessment of the ability of gold-bearing ore for processing/enrichment. The visualization of particular grains under the SEM allowed to estimate the amount of released gold particles, as well as to find the real dimensions and morphology of these particles (Chanturiya et al., 1997).

As one can see, the methods presented above are of common character and can be adapted, apart from mineralogy and geology, in many branches, including the mineral processing.

In this paper the possibilities of application and the results produced basing on the scanning electron microscopy examination and X-ray diffraction analysis are shown. These methods were used to control the efficiency of the new chemical flotation technology of carbonate copper ore processing in KGHM Polska Miedź" S.A.

2 THE CHEMICAL - FLOTATION METHOD OF ENRICHMENT

The chemical – flotation enrichment consists in the decomposition of carbonate dead minerals, in which the useful minerals occur as impregnating inclusions, by use of sulphuric acid. In such a way the useful minerals in the form of sulphides are precisely liberated; the carbonate matrix covering them and hampering the flotation is thus dissolved. The application of this method in preparation of material as a feed to the further flotation is an alternative to the additional grinding in tumbling mills. Grinding before the copper ore enrichment is in these conditions poorly effective and not recommended from the economy view point.

The mineralogical examination of products proves that at least 70% of copper minerals being the wastes in classic enrichment technology, despite very fine grinding, occur as intergrowth and inclusions. Therefore the chemical modification of the material fed to the flotation process is advisable and effective.

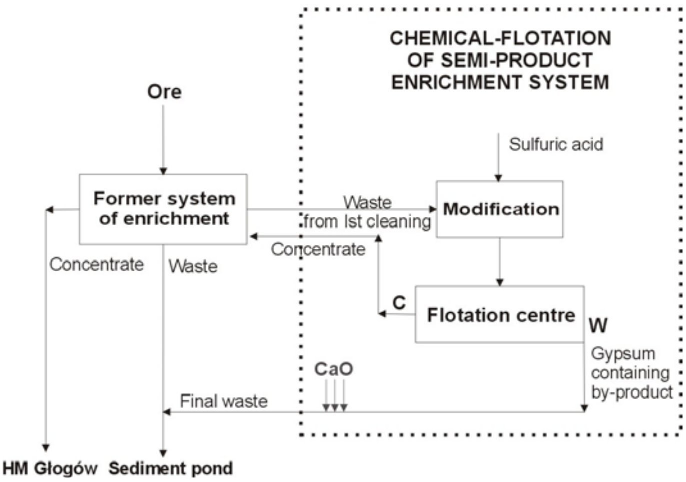

Figure 1. Block diagram of chemical – flotation enrichment technology

Implementation of this process does not imply any significant changes in the systems of enrichment installed, apart from the separation of waste stream from the first cleaning and its further modification. In Figure 1 the block diagram of this operation is drawn. The material output from the cleaning flotation circuit is subjected to the digestion by acid and then, as a modified and better enriched, it is turned back to the same circuit.

The chemical process of ore modification (leaching) before the flotation is based upon the intensive reaction of the sulphuric acid (H_2SO_4) with calcium and magnesium carbonates. These compounds are among the most important constituents of the dead rock and occur as poorly processed or hardly susceptible to the flotation intergrowth with ore minerals, forming so-called sludge covers on their surface, hindering the flotation.

The reactions between the sulphuric acid and calcite or dolomite are as follows:

- reaction of sulphuric acid with calcite ($CaCO_3$):

$$CaCO_3 + H_2SO_4 + 2H_2O \rightarrow$$
$$CaSO_4{\cdot}2H_2O + CO_2\uparrow + H_2O$$

- reaction of sulphuric acid with dolomite ($CaCO_3{\cdot}MgCO_3$):

$$CaCO_3{\cdot}MgCO_3 + 2H_2SO_4 + 9H_2O \rightarrow$$
$$CaSO_4{\cdot}2H_2O + MgSO_4 + 9H_2O + 2CO_2\uparrow$$

The decomposition products of carbonates in this modification process are precipitated calcium sulphate and soluble magnesium sulphate, as well as gaseous carbon dioxide. The non-oxidizing conditions of leaching and non-stoichiometric deficiency of acid prevent the digestion of sulphide minerals and transport of copper to the solution. In such a way the pH of suspension after leaching becomes soon after enough high that this suspension can be brought toward the flotation installation, without corrosion hazard.

3 MATERIALS AND METHODS

The samples collected during the control of the new technology were examined. The material was produced as a result of the waste from the Ist cleaning modification by H_2SO_4. In Figure 2 a diagram of the modified material enrichment is shown. The point of sample collection is indicated. In this scheme the de-gypsum and main flotation, being the part of the "chemical – flotation of semi-product enrichment system" are shown, as well as the cleaning flotation, being the part of "formerly existing system" (Fig. 1).

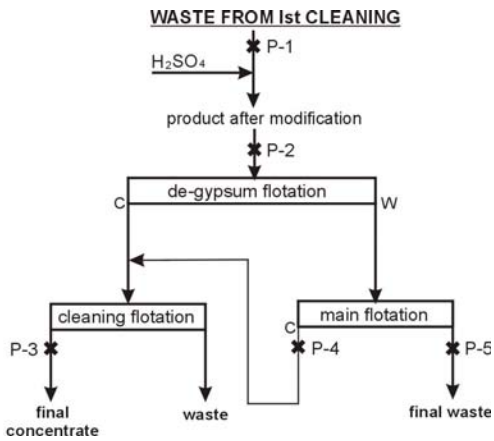

Figure 2. Diagram of enrichment with marked points of sample collection

The five different products of the process samples were examined; their characteristics are given in Table 1.

Table 1. Cu, Ag and Au contents in particular products

Product	Cu [%]	Ag [g/Mg]	Au [g/Mg]
P-1 (waste from I cleaning)	1.68	40	0.030
P-2 (after modification with H_2SO_4)	1.14	32	0.022
P-3 (final concentrate)	25.13	477	0.900
P-4 (concentrate from main flotation)	2.56	56	0.048
P-5 (final waste)	0.17	3	0.009

All samples were examined using following procedures:
- observations under the scanning electron microscope; analysis of microstructure in selected areas;
- distribution of particular elements in selected areas (mapping);
- energy dispersive analysis by X-rays in selected points;
- phase composition of samples by X-ray diffraction analysis.

4 RESULTS

The results thus produced allow for a reliable analysis and assessment of particular products originated from the new method of enrichment. In subsequent figures (Figs 3-9) the SEM micrographs and XRD patterns of samples are presented. Because of a huge amount of analyses, only those representative ones are given as examples illustrating the problem. However, the conclusions are drawn from all the data. Their interpretation allowed for gaining information, as the composition and the effect of technology implemented in this project were concerned.

Some results relating to the particular samples are presented below.

P-1 – waste from the 1st cleaning; 1.68% Cu; on SEM micrographs one can notice a substantial amount of calcite $CaCO_3$ grains (occurring as crystals of large dimensions, a variety of forms), quartz SiO_2, halite NaCl and copper sulfides, as well such elements as Mg, Al.

P-2 – product after the modification with sulfuric acid; 1.14% Cu; the characteristic needle-like forms are observed; they correspond to the increase of gypsum $CaSO_4{\cdot}2H_2O$ content (Fig. 4). Gypsum occurs as well developed plate-like and fibrous crystals; it can be easily distinguished on SEM micrographs. Among the other constituents there are also quartz SiO_2 and ankerite $Ca(Mg, Fe)CO_3$, on the other micrographs there are also copper sulfides as well as some amount of elements, such as Al, K, Na, Cl.

P-3 – final concentrate; 25.13% Cu; copper sulphides rarely form single crystals and they are difficult to separate, they preferably occur as fine-grained aggregates. As it can be derived from the XRD pattern (Fig. 6) the two other copper sulphides are present: covelline and djurleite, moreover, the quartz, montmorillonite, calcite and gypsum are detected. The occurrence of djurleite, a mineral of poor content in copper ore, is the best prove for accuracy of this method. SEM micrographs reveal also the presence of iron sulphides.

P-4 – concentrate from the main flotation; 2.56% Cu; the characteristic minerals as detected by XRD are: quartz, dolomite and gypsum. The mapping visualization gives the assemblages of copper and iron.

P-5 – final waste; 0.17% Cu; both XRD patterns SEM micrographs and EDS maps exhibit the dominating occurrence of quartz and calcite. There are also S, Mg, Al and Cl.

The results and their analysis prove the increasing content of free copper sulphide in the product after the modification by sulphuric acid, as compared to the composition before modification.

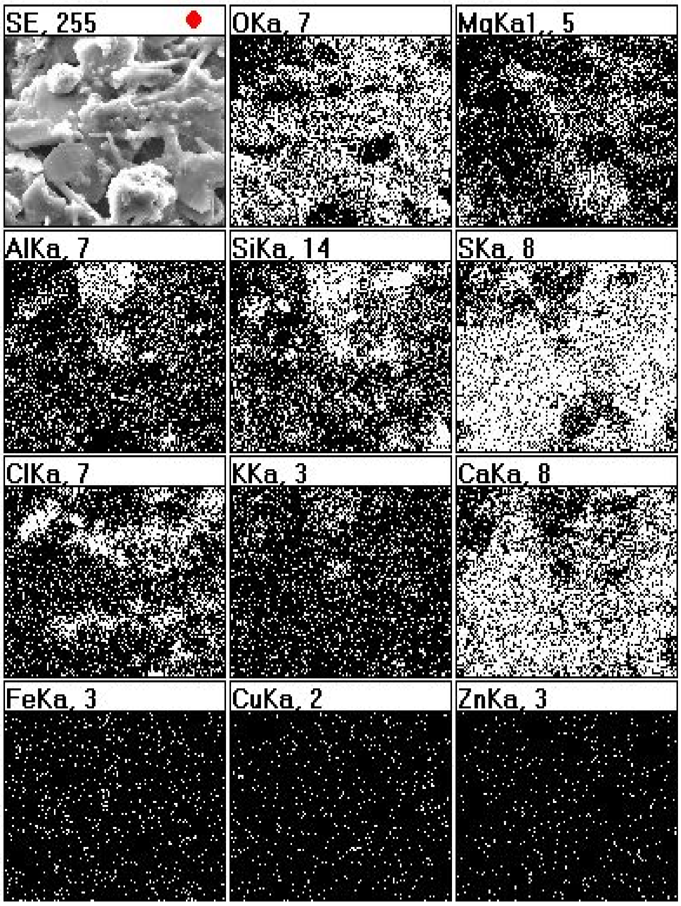

Figure 3. EDS map of particular elements distribution in the selected area of sample P-2

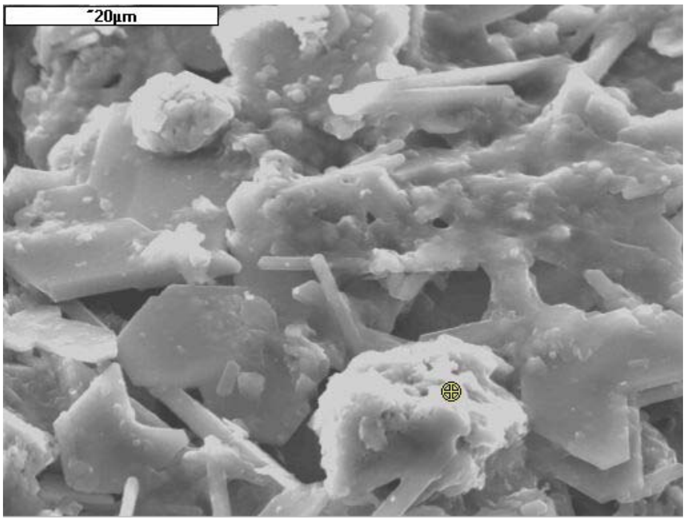

Figure 4. SEM microstructure of the selected area of sample P-2

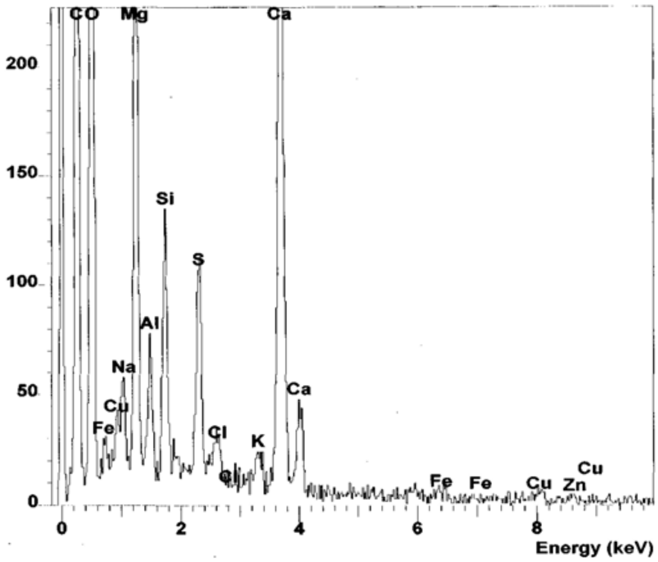

Figure 5. EDS plot showing the presence of particular elements distribution in an analyzed spot of sample P-2

No	d_Fit(A1)	2Θ	I_{Net}	PDF-No	FWHM	H K L
1	4.4658	19.8649	3.88	29-1498	0.2579	1 0 0
2	4.4658	19.8649	3.88	34- 660	0.2579	6 0 0
3	4.2664	20.8037	3.85	33- 311	0.2709	0 2 1
4	4.2664	20.8037	3.85	34- 660	0.2709	3 3 1
5	4.2664	20.8037	7.71	46-1045	0.2709	1 0 0
6	3.3399	26.6687	39.21	46-1045	0.1381	1 0 1
7	3.3399	26.6687	39.21	6- 464	0.1381	1 0 0
8	3.3399	26.6687	78.43	34- 660	0.1381	-1 3 3
9	3.0295	29.4603	16.02	5- 586	0.2114	1 0 4
10	3.0295	29.4603	16.02	6- 464	0.2114	1 0 2
11	3.0295	29.4603	32.04	34- 660	0.2114	-4 3 3
12	2.9646	30.1202	28.99	34- 660	0.2864	-4 0 4
13	2.8990	30.8188	58.52	35- 667	0.3413	1 0 4
14	2.8990	30.8188	58.52	34- 660	0.3413	6 2 3
15	2.8166	31.7438	52.29	34- 660	0.1498	-9 1 1
16	2.8166	31.7438	52.29	6- 464	0.1498	1 0 3
17	2.5576	35.0565	3.88	29-1498	0.3064	1 0 5
18	2.5576	35.0565	3.88	34- 660	0.3064	8 4 0
19	2.5576	35.0565	7.76	35- 667	0.3064	0 1 5
20	2.3892	37.6174	27.18	34- 660	0.4846	11 1 0

Figure 6. XRD pattern of sample P-3 together with the set of XRD data (interplanar spacings *d*, intensity *I*, *hkl* indices, PDF-No identification charts)

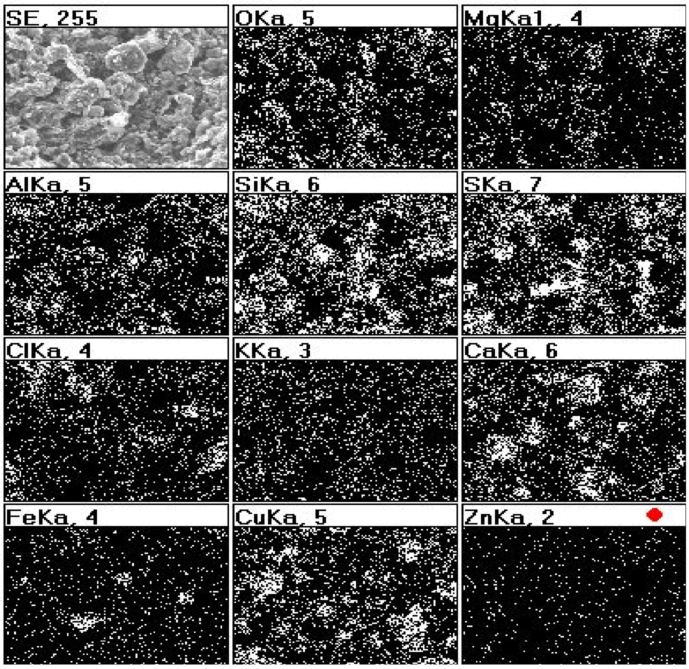

Figure 7. EDS map of particular elements distribution in the selected area of sample P-3

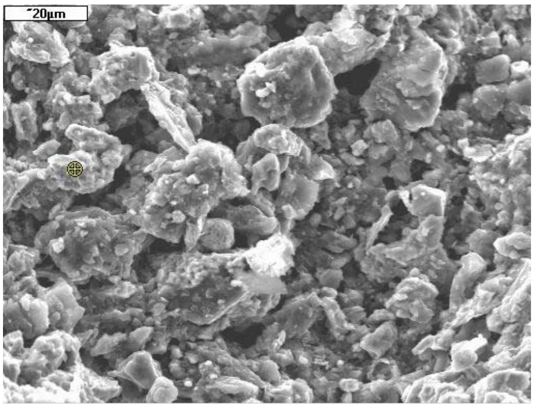

Figure 8. SEM microstructure of the selected area of sample P-3

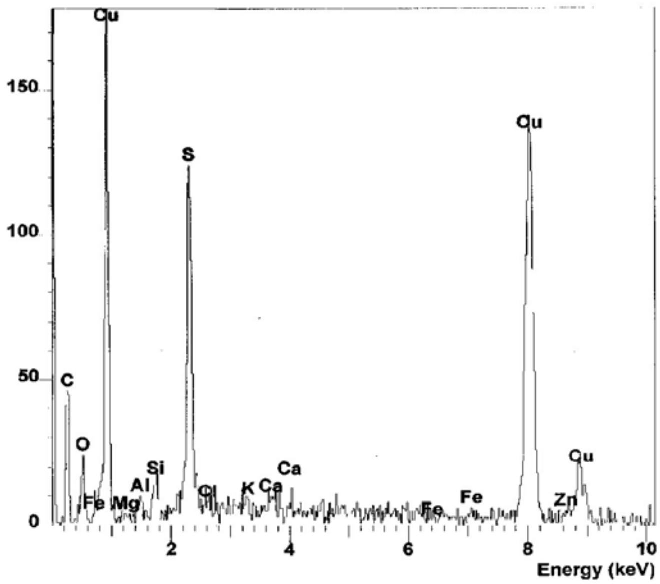

Figure 9. EDS plot showing the presence of particular elements distribution in an analyzed spot of sample P-3

5 CONCLUSIONS

The new method of copper ore enrichment, the experimental procedures applied in its assessment and the results of tests for copper ore processed materials from industrial practice has been presented in this work.

The results thus obtained: SEM micrographs, EDS maps and plots, XRD patterns gives valuable data as a mineral composition, chemical composition and morphology of samples is concerned (surface effects, shape and continuity of structural elements, nature and size of inclusions, defects). This information can prove the occurrence of particular element or mineral, as well as became a basis for their recovery.

The knowledge thus obtained can serve when the way of ore preparation is considered and the optimum method of ore enrichment is selected, as well as the efficiency of the process is assessed.

The associated application of the both methods: scanning electron microscopy and X-ray diffraction analysis can be particularly profitable for the better examination of the post-flotation wastes generated in the processing department of the mining and metallurgical company KGHM Polska Miedź S.A. The annual output of waste stored in the sediment pond is about 28 Mg and the copper content is on the level about 0.17-0.24% Cu. The full assessment of copper, as well as the form of Cu and other elements occurrence can result in research projects aimed in their better processing to avoid the further loss of valuable raw materials.

The methods of examination should be complementary and confirming. The simultaneous application of the techniques mentioned above was fructuous. The occurrence of investigated elements documented by SEM/EDS was confirmed by XRD phase studies.

The further research works by means of the methods used in this report, as well as the other modern techniques, can contribute to the development of future copper recovery technology from the post-flotation wastes.

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