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# REFRACTORY POLYMETALLIC ORES BY FLOTATION. DIRECTIONS FOR IMPROVING METALLURGICAL BALANCE

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**ABSTRACT** – The beneficiation complexity of the lead-zinc ore from the Shalkiya deposit is associated with the fine dissemination of galena and sphalerite, a high zinc module, and the presence of carbonaceous material. The flotation kinetics of carbonaceous material, galena, and sphalerite under different reagent regimes have been studied. Apolar and sulfhydryl collectors, as well as flotation depressants for carbonaceous material based on lignosulfonates, have been tested. The composition and surface properties of the carbonaceous material were analyzed using elemental composition analysis, X-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy, and acid-base centers characterization. A rational collective-selective flotation scheme has been substantiated.

**Keywords:** Flotation, Galena, Sphalerite, Carbonaceous Material, Reagent Regime.

## INTRODUCTION

The main useful minerals in the ores of the Shalkiya deposit are sphalerite, galena and pyrite, which have phenocrysts from dusty to 0.1 mm and are characterized by close intergrowth between themselves, as well as with minerals of waste rock, in particular quartz and carbonates. The very fine phenocrysts of lead and zinc minerals are complicated by the presence of carbonaceous matter, which is present both in the host rocks and in the useful minerals. In earlier studies on the development of ore enrichment technology of the Shalkiya deposit were proposed collective-selective and selective flotation schemes [1,2].

Glembotsky V.A. and Dmitrieva G.M. studied 28 galena samples with a lead content ranging from 86.07% to 62.16% [3], However, no clear correlation between conductivity

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type and galena flotation activity was identified. The authors distinguished two groups of galena. The first group contains a minimal amount of impurities, allowing it to actively interact with ethyl xanthate and dithiophosphate. The second group is characterized by increased surface heterogeneity and a greater tendency to oxidation, which results in weak interaction with ethyl xanthate and resistance to flotation by dithiophosphates.

In recent decades, in addition to the known factors affecting the flotation properties of sulfides—such as the impurity composition of minerals, the degree of surface oxidation, and the presence of pyrite—the presence of carbonaceous material in ores has also been recognized as an influencing factor. This further affects the selection of the reagent regime and the flotation scheme [4-6].

Carbonaceous material, which belongs to naturally hydrophobic multiphase minerals [7], leads to significant mutual losses of galena and sphalerite between the commercial concentrates.

## EXPERIMENTAL

### Materials and Methods

*Materials*

The mineral composition of the sample, calculated on the basis of the data of microscopic studies, X-ray spectral and mass spectrometric analysis, is given in **Table 1.** Ore minerals are represented by galena, sphalerite, and pyrite. The host rocks are represented by quartz and carbonates (dolomite and calcite), the ore also contains small amounts of carbonaceous matter, feldspars, and muscovite.

**Table 1** Mineral composition of the sample

| Mineral Group | Content, wt. % | Mineral Group | Content, wt. % |
|---|---|---|---|
| Galena | 1.57 | Sulfides ($FeS_2$, $CuFeS_2$, $Cu_{12}As_4S_{13}$) | 4.28 |
| Sphalerite | 6.94 | Mica and clay minerals (muscovite, kaolinite, chlorite) | 3.38 |
| Smithsonite | 0.02 | Iron hydroxides | 0.23 |
| Quartz | 38.13 | Other barren minerals | 0.17 |
| Carbonates | 43.97 | Carbonaceous matter | 1.30 |

According to MLA data, the main mineral concentrators of elements are:

- zinc: sphalerite and carbonates with a distribution of 87.44% and 8.04%, respectively;
- lead: galena and carbonates with a distribution of 86.99% and 10.64%, respectively.

Sulfide fractions were prepared from hand specimens by manual grinding in an agate mortar and dry classification. The -10 μm fraction was removed using a wet sedimentation method based on settling velocity.

Before flotation or adsorption, sulfide samples were soaked in 1% NaOH solution for 24 hours and then rinsed with distilled water in five specific volumes until reaching a neutral pH. The carbonaceous material was separated by flotation in a mechanical

flotation machine without collectors or frothers, then dried and fractionated into narrow size classes.

*Methods*

Figure 1 shows the IR spectrum region of the carbonaceous material extracted from lead-zinc ore from the Shalkiya deposit.

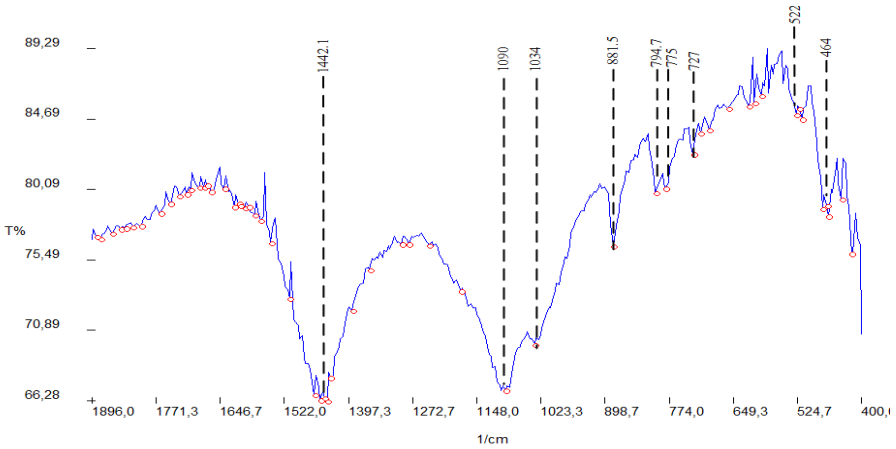


**Figure 1** Transmission IR spectrum of carbonaceous material (±2 $cm^{-1}$)

**Characteristic Bands**

A strong absorption band with a transmission minimum at 1452 and 1440 $cm^{-1}$ corresponds to C-O stretching vibrations (vCO) at the carbonates. A strong band with minima at 1090 and 1034 $cm^{-1}$ is associated with Si-O stretching vibrations. The bands at 881.5 $cm^{-1}$, the doublet at 794.7 and 775 $cm^{-1}$, and bands of varying intensity at 727, 522, and 464 $cm^{-1}$ correspond to deformation and out-of-plane vibrations of X-O bonds, where X may represent Si, C, or other elements present in the carbonaceous sample. The IR spectra of the carbonaceous material from the ore, based on the main characteristic bands, are consistent with the IR spectrum presented in the study by Lee et al. (2023). [7] Table 2 presents the characteristics of sulfides and carbonaceous material. The chemical composition was determined using X-ray fluorescence spectrometry (XRF) (Shimadzu XRF-1800 spectrophotometer, Japan). The specific surface area of the fractions was measured using the low-temperature nitrogen adsorption method (BET) (Nova 2200E, Quantachrome Instruments, USA).

XPspectroscopy was used for a specific fracture -100 +44 µm of the samples in order to define the elemental composition of carbonaceous samples surface layer at 2 nm depth and to define oxygen and carbon state in coal and graphite. The research was done using X-ray photoelectronic spectrometer PHI5000VersaProbeII (ULVAC-PHI).

A narrow fraction (-71 +41 µm) of sulfides and carbonaceous material was studied. The reagent addition sequence in the mechanical flotation machine chamber followed the procedure described in Section 1.2.

**Table 2** Chemical composition of galena, sphalerite, and carbonaceous material (CM)

| Sample | Fraction, μm | Specific surface area, $m^2/g$, ± 2.00 | Elemental composition, % ±0.02 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Pb | Zn | S | Fe | Cu | Cd | Al | Si | C ±2.0 | other | Total |
| PbS | -44 +10 | 0.52 | 83.86 | 1.17 | 12.65 | 0.69 | 0.13 | - | 0.04 | 0.19 | - | 1.26 | 100.00 |
| | -71 +41 | abs | | | | | | | | | | | |
| ZnS | -44 +10 | 0.86 | 1.50 | 63.10 | 31.07 | 1.20 | 0.10 | 0.40 | 0.03 | 0.90 | - | 1.70 | 100.00 |
| | -71 +41 | abs | | | | | | | | | | | |

| Carbonaceous material | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Fraction, μm | Specific surface area, $m^2/g$, ± 2.00 | Elemental composition, % | | | | | | |
| | | C ±2.0 | H ±3.1 | N ±0.2 | O ±0.5 | S 0.2 | Ash content A, %, ± 0.5 | Total |
| -71 +41 | 12.93 | 10.2 | - | - | 4.7 | 0.7 | 84.4 | 100.00 |

Concentrate fractions were collected at 0.1, 0.5, 1, 2, 3, and 5 minutes. The flotation rate constant (k, $min^{-1}$) for the fast-floating fraction (flotation duration of 1 minute) was determined graphically as the slope of the straight line in the coordinates ln(100/(100-ε)) = f(t).

For direct definition of Lewis-Bronsted active acid-base centers on surface Gammet indicators with different $pK_a$ values were used [8-10]. Table 3 shows the characteristics of the Gammet indicators used to define types of acid-base centers on the surface of studied carbonaceous samples based on Gammet indicator adsorption.

**Table 3** Gammet indicators' characteristics to define types of acid-base centers

| Indicator | Formula | Molecular mass | λ, nm | pKa | Active center type |
|---|---|---|---|---|---|
| Bromocresol purple | $C_{21}H_{16}Br_2O_5S$ | 540.22 | 590 | 6.4 | Bronsted acid |
| Bromthymol blue | $C_{27}H_{28}Br_2O_5S$ | 624.39 | 610 | 7.3 | Bronsted base |

Spectophotometer UV-VIS-NIR Cary 6000i by Agilent Technologies (USA) with wave range 175 to 1800 nm was used to control characteristic strip absorption intensity before and after interaction with the carbonaceous sample.

## RESULTS AND DISCUSSION

Panoramic specters (Figure 3) prove impurities' content for the surface of carbonaceous material (CM) recovered from sulphidic ore.

Table 4 shows elemental composition of studied samples' surface.

**Table 4** Sample surface elemental composition, ± standard edviation, %

| Sample | C ±1.0 | O ±1.0 | Si ±0.5 | Mg ±0.5 | Al ±0.5 | Ca ±0.5 | Zn ±0.5 | Fe ±0.3 | S ±0.2 | Pb ±0.1 |
|---|---|---|---|---|---|---|---|---|---|---|
| CM | 49.2 | 34.5 | 5.1 | 2.5 | 1.9 | 2.5 | 2.8 | 0.4 | 0.7 | 0.4 |

### The flotation kinetics

The flotation of a narrow-size monomineral fraction of sulfides and CM under different preparation conditions for research are presented in Figure 4. Butyl xanthate

(KButX) was selected as the sulfhydryl collector, while fuel oil (FO) used as the non-polar reagent.

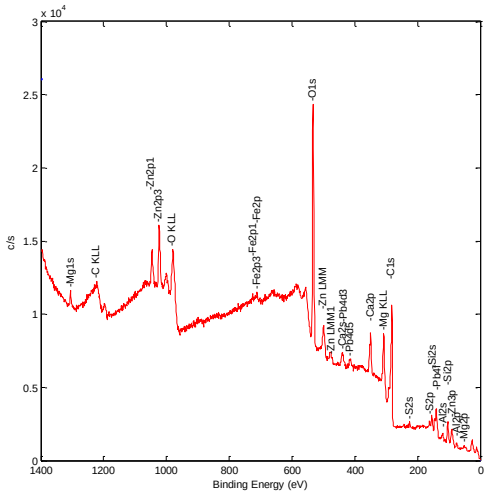


**Figure 3** Panoramic XPS specters of carbonaceous material (CM) sample from polymetal sulphidic ore

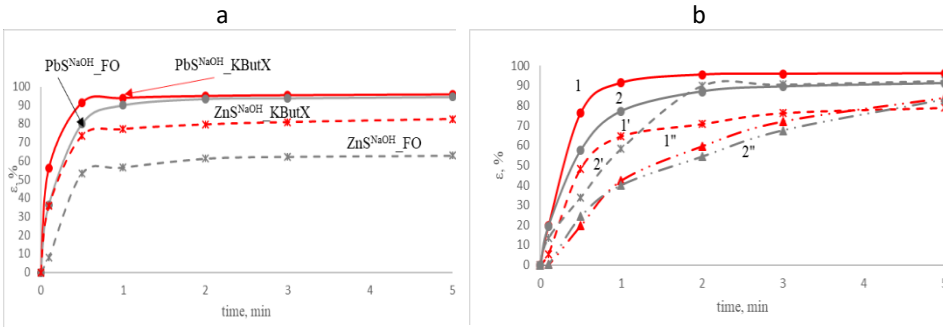


**Figure 4** The flotation kinetics of PbS (1,2), ZnS (1',2') and CM (1",2") by KButX (1, 1', 1") and FO (2,2',2") under different preparation conditions of sulfides
[$C_{init}$ (KButX) $10^{-4}$ M (18 mg/l), FO 50 mg/l, PO 10 mg/l
a - with pre-treatment NaOH; b - without pre-treatment]

Preliminary alkaline treatment of sulfides demonstrates increased floatability of PbS with KButX (εPbS = 91% in 0.5 min) in comparison with ZnS (εZnS = 61% in 2 min). The flotation activity of galena with FO in the concentrate is higher than that of sphalerite (εPbS = 90.1% in 1 min and εZnS = 77.1% in 1 min).

Aged sulfides (figure 4a) showed high flotation activity for galena with KButX (εPbS=96% in 0.5 min) and sphalerite (εZnS = 76.2% in 3 min), as well as with the apolar collector (εPbS = 89.5% in 2 min and εZnS = 84%). The carbonaceous material demonstrated lower floatability, with both collectors achieving similar recovery levels

(εCM = 74% in 4 min). The flotoability of aged sulfides and CM in terms of recovery is comparable, suggesting that their separation may be obstructing.

The flotation kinetics of fast floating fraction was defined graphically with flotation duration of 1 min. the data are presented in Table 5.

**Table 5** The flotation parameters of sulfides and CM with a flotation duration of 1 min

| The reagent regimes | k, $min^{-1}$ | $\varepsilon_{max}$, % | The reagent regimes | k, $min^{-1}$ | $\varepsilon_{max}$, % |
|---|---|---|---|---|---|
| Without preprocessing | | | | | |
| PbS_KButX | 2.46 | 91.4 | CM_FO | 0.56 | 40.0 |
| ZnS_KButX | 1.08 | 64.5 | PbS_FO_LS | 1.21 | 54.6 |
| CM_KButX | 0.61 | 42.4 | ZnS_FO_LS | 0.74 | 17.7 |
| PbS_FO | 1.71 | 88.3 | CM_FO_LS | 0.16 | 77.9 |
| ZnS_FO | 1.25 | 77.1 | | | |
| With NaOH and rinsing | | | | | |
| $PbS_{NaOH}$_KButX | 2.11 | 93.8 | $PbS_{NaOH}$_FO | 2.04 | 90.1 |
| $ZnS_{NaOH}$_KButX | 0.81 | 56.6 | $ZnS_{NaOH}$_FO | 1.12 | 77.1 |

The rate constant of galena decreases slightly, while that of sphalerite decreases significantly, when carbonaceous material depressors are used during the flotation of primary ores. When carbonaceous material depressors are used, the flotation rate constant decreases only during the first 2 minutes. However, with the increase in flotation time, the flotation kinetics rises, and the maximum recovery reaches at least 50% after 5 minutes of flotation

The results of the determination of acid-base centers in the investigated pH range during flotation and adsorption are presented in table 6.

**Table 6** The results of dtermination of acid-base centers in the pH range of 6-8

| Sample | PbS | ZnS | CM |
|---|---|---|---|
| Bronsted acid pKa=6.4, µmol/$m^2$ | 3.0 | 4.3 | 0.3 |
| Bronsted base pKa=7.3, µmol/$m^2$ | 25.3 | 10.0 | 4.4 |

The active surface centers in the investigated pH range mainly correspond to Bronsted bases. They act as donors in donor-acceptor interactions. It can be assumed that surface reactions occur with nonionic collectors containing unsaturated bonds or that they promote xanthate formation through dixanthogen.

The following mechanism of interaction of lignosulphonates with surface of the separated minerals and CM is assumed based on experimental data. Carbonaceous material (CM) interacts strongly with lignosulphonates due to its complex surface structure such as silicates, carbonates and hydrophobic carbon films. At near neutral pH, surface metal hydroxide groups (e.g. Al-OH, Ca-OH) remain protonated and thus positively charged or amphoteric. This promotes electrostatic attraction with anionic sulphonate groups of lignosulphonates. In addition, hydrophobic interactions with carbon-rich domains contribute to adsorption. Despite this, CM recovery could not be reduced below 50%, indicating persistent flotation activity due to residual hydrophobic sites. Galena (PbS) retains strong flotation activity due to the highest Brønsted base site

density (25.3 μmol/m²). At pH ~6.4-7.3 the surface is less oxidised and more reactive, but shows limited affinity for lignosulphonates. This is probably due to lower surface heterogeneity and a dominance of $Pb^{2+}$ rather than hydroxylated species. As a result, galena remained effectively floatable. Sphalerite (ZnS), primarily in cleiophane form, has fewer surface base sites (10.0 μmol/m²) and a higher tendency toward surface hydroxylation or oxidation. At near-neutral pH, $Zn(OH)^{+}$-type sites can facilitate moderate lignosulphonate adsorption, resulting in reduced flotation rate but insufficient depression for selective separation. Thus, in the pH range 6.4-7.3, lignosulfonates are partially effective as depressants, but selective suppression of CM is not achieved.

Taking these factors into account, the established dependencies provide a solid basis for the selection of collective selective flotation technology for lead-zinc sulphide ores, where it is advisable to remove the carbonaceous material prior to collective flotation.

## CONCLUSION

It has been experimentally shown, that the weathered low-iron modification of sphalerite (cleiophane) floats similarly to galena, including using of FO in reagent regimes. Alkaline treatments of the galena and sphalerite surfaces before flotation allows achieving the expected flotation results – galena floats faster and higher than sphalerite.

Flotation kinetics of galena, sphalerite, and carbonaceous material with butyl xanthate and fuel oil, both individually and in the presence of carbonaceous material depressors and lignosulfonates, demonstrated the inability to achieve selective depression of the carbonaceous material compared to galena and sphalerite, as recovery below 50% could not be achieved.

The obtained results on monomineral fractions of cleiophane, galena and carbonaceous material made it possible to determine the reason for the low process efficiency of direct selective flotation without the removal of carbonaceous material at the Shalkiya deposit. This is due to the low contrast in the flotation properties of cleiophane and galena.

Due to the multiphase nature of the carbonaceous material and the obtained flotation kinetics results, it is advisable to remove the carbonaceous material prior to collective flotation. The established dependencies serve as the basis for selecting a collective-selective flotation technology for lead–zinc sulfide ores, in which the finely disseminated sphalerite grains are present as cleiophane.

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