A.O. Teut¹ , N.A. Kulenova²

¹The Eastern Mining and Metallurgical Research Institute for Non-Ferrous Metals (VNIITSVETMET), 1, Promyshlennaya Str., Ust-Kamenogorsk, 070002, Republic Kazakhstan ²D. Serikbayev East Kazakhstan State Technical University, 19, Serikbayaev Str., Ust-Kamenogorsk, 070012, Republic Kazakhstan *A.O. Teut N.A. Kulenova*

THE ROLE OF THERMOELECTRICITY IN SELF-ORGANIZATION PROCESSES OF POLYSULFIDE ORES

The purpose of this work was to study the correlation between the electrical and chemical parameters of ore bodies and their role in the restoration of geosystem balanced state. The investigation was concerned with studying the material composition, the electrical and thermal properties of polysulfide ores and the laws of their change with a destabilization of geological formation. A close correlation between the electrophysical and electrochemical properties of sulfide materials has been established. It has been shown that synergism effects contribute to restoration of a disbalance between the material and energy components of the ore system due to development of electrochemical reactions and thermoelectric effect resulting in the active *formation of oxidation zone. The results of research can be used to control the processes of crude ore treatment and to prevent its self-ignition.*

Key words: polysulfides, synergism, oxidation zone, geosystem stability, electric dipole, galvanocouple, thermoEMF.

Introduction

Natural bodies, including geological ones, by definition of academician V.I. Vernadsky, are formations combining two substances: material and energy. They are in close correlation and, under stable external conditions, in a balanced state. With a change of external conditions in the natural systems, this balance is disturbed, bringing about the processes aimed at its restoration with a new state of environment. The synergetic effects are distinctly traced by the results of analysis of the material characteristics of ore bodies, their composing ore minerals, the electrophysical, electrochemical properties of these formations and the electrical fields produced by them [1, 2].

The nature of energy effects

There are two main types of reasons for destabilization of geological systems: natural, related to development of different geodynamic, metamorphological, etc. processes, and antropogenic, caused by human technological activity.

Ore accumulations and bodies of pyrite-polymetal deposits are nonuniform in the distribution of material and physico-chemical parameters in them, which is caused by polygenesis and polychronism of their formation. When ore bodies of deposits are formed in several stages, the distribution of ores in them has a zone structure, in the form of stripes or layers. In so doing, the ore materials in each zone are characterized by their unique physico-chemical properties leading to a drastic difference in the electrophysical properties of the layers formed. Owing to this, in terms of energy, they are natural thermoelectric elements combined with micro- and macrogalvanic elements located on different hierarchical levels. In the open environment such thermoelectric elements are generally arranged in subconformity with the occurrence of the ore bodies. The higher is temperature difference on the ends of these elements, the higher is thermoelectromotive force with which they generate current.

For many millions of years the established deposits have been under stable conditions with a balanced state between the material and energy components. In the case of blind ore bodies the difference in temperatures between the upper and lower parts is determined by the temperature gradient of the Earth. Under Rudny Altai conditions this temperature difference with a vertical drop of the ore body and its length to 2 km is 20 to 30 °С. With such temperature difference, the intensity of emerging electrical field does not exceed tenths of a microvolt and thermal currents are minor.

Reaching the erosive truncation changes the environmental conditions (humidity, oxygen concentration, etc.) for micro- and macrogalvanic elements which initiates development of electrochemical reactions with formation of secondary minerals. This process is accompanied by heat release and heating up the upper part of ore body to temperature beyond $100 - 150$ °C (almost fivefold increase). Creation of high-power thermal gradient results in the origination of considerable thermoelectric effect and re-formation of natural dipole electrical system: position of ore body heating area is changed and potential difference of the upper and lower dipoles is increased considerably. In the former case heating area was concentrated in the fringe zone, whereas in the latter case it migrates to the head of the ore body. In so doing, due to a large temperature difference between the upper and lower areas of the ore bodies, the intensity of natural electrical field is much in excess of the intensity of electrical fields of the ore bodies that are in a stable state. Such deposits have a well-developed oxidation zone whose formation is related to bringing the material and energy components into a balanced state and which is frequently a seat of sulfide fires.

Antropogenic reasons leading to destabilization of geological systems during extraction and treatment of ores are represented by a continuous process including consecutive steps of development of ore bodies and accumulations by mining; storing of mass in the stockpiles of mines and dressing works; preparation of charge for dressing; dressing; subsequent treatment.

Development of ore accumulation by mining brings about synergism effects similar to those that emerge when an ore body reaches the erosive truncation. Synergism is most conspicuous in places of self-ignition of ores. These processes first appear in the ores enriched with microgalvanic elements. The temperature in places of ignition reaches $90 - 110$ °C, which contributes to launching of local thermoelements. Thermal currents resulting from the work of thermoelectric element, in turn, produce a significant influence on the work of micro- and macrogalvanic elements and intensify oxidation processes. The work of described system of electric elements results in formation of secondary minerals.

Ore excavation disturbs the balance between the material and energy components in total break pieces. Transition to a new stable state during this stage is accompanied by self-organization processes aimed at establishing the balance by transformation of material component due to the effect of micro- and macrogalvanic elements. Transformation of material component changes, in turn, the energy component, cancelling part of natural galvanic elements.

Synergism effects are also observed in the ore stacks of homogenizing yards at the mines and dressing works with a layer by layer formation of ores with different electrophysical (electrochemical)

properties. Crushing and grinding of ores being prepared for flotation enlarges the total surface of natural galvanic elements which intensifies their work.

Results of research on the composition and properties of ores

This paper presents the results of research on pyrite-polymetal and gold-sulfide deposits of Rudny Altai which are notable for their polygenetic nature. It is shown [3, 4] that each step of formation of such deposits took place under specific thermobarogeochemical conditions, unique to this step. This determined zonal distribution of the natural types of ores within ore bodies, as well as the polymorphism of same-name minerals and, hence, the impurity composition and quantitative relations of impurities therein. In Tables 1 and 2 are given compositions of various types of ores and impurity distribution in the depth of occurrence of the ore deposit. Deviations of crystal lattice shape of minerals (including same-name) from perfect one, as well as different composition of impurities in them account for the difference in their electrophysical properties.

Table 1

Chemical composition of typical ores of East Kazakhstan gold-bearing deposits

According to their electrophysical properties, sulfide minerals are classified as semiconductors. This is directly related to the Fermi level position in the surface layers of mineral-semiconductors which determines such important surface characteristic as electrode potential representing potential drop at the interface of mineral and ionic medium (for instance, leaching solution) or other mineral forming an aggregate with it.

Table 2

Tables 3 and 4 present the electrophysical properties of the ore minerals of the main deposits of Rudny Altai [5]. The estimates of semiconductor properties of minerals were made on the basis of results of measuring the thermoelectric, galvanomagnetic effects, the electrical conductivity and studying the volt-ampere characteristic of minerals. As can be seen, the thermoEMF T_{EMF} and electrical resistivity ρ of minerals vary within wide limits. The largest variation range is peculiar to iron sulfides (pyrite, markasite) composing, as a rule, a matrix of pyrite-polymetal and gold-sulfide ores (from 60 to 95% of mineral composition). Among them there are species possessing both electron- and hole-type conductivity.

Chalcopyrites are mostly characterized by electron-type conductivity. Grains with hole-type conductivity are extremely rare in the metamorphized ores of the Maleyevskoye deposit.

Among the ores of studied deposits, galenite mainly possesses the electron-type conductivity. Grains with hole-type conductivity are sometimes found in the ores of the Orlovskoye, Maleyevskoye and Tishinskoye deposits.

Table 3

Electrophysical properties of the main ore minerals of the Nikolayevskoye and Orlovskoye deposits

* – is of limited occurrence.

ThermoEMF of sphalerites rarely exceeds tenths and even hundredths of mV/degree. In so doing, the hole-type conductivity is mostly recorded. In the ores of the Nilolayevskoye deposit the varieties of sphalerite are sometimes found (marmatite with increased iron content), characterized by thermoEMF value within 5 to 9 mV/degree.

Table 4

Electrophysical properties of the main ore minerals of the Tishinskoye and Maleyevskoye deposits

Thus, ores under study are a complex electrode "composed of individual mineral electrodes having relatively positive and negative values of electrode potential" [6]. In so doing, the minerals electrochemically interact and form complex microgalvanic elements. Experimental studies aimed at simulating the work of galvanic elements formed by natural mineral aggregates have shown [5] that electrode potentials of grains as part of polymineral ores differ considerably from steady-state potentials of isolated monominerals (Table 5).

Table 5

Effect of "sphalerite – chalcopyrite" galvanic element from the ores of the Nikolayevskoye deposit on passing of copper and zinc into solution

From Table 5 it is seen that with formation of a short-circuited galvanocouple (experiment 1) passing of copper and zinc into solution is increased almost twofold as compared to separate leaching of chalcopyrite and sphalerite (experiments 3 and 4). Some increase of extraction of metals to solution with a simultaneous location in it of non-contacting electrodes of chalcopyrite and sphalerite (experiment 2) is apparently related to formation of ionic electrical bond. Fig. 1 shows a change in electrode potentials on different mineral electrodes in acid and alkali media. The run of potential curves indicates that the work of galvanocouples is controlled by anode process which is retarded both due to products of direct oxidation of sulfides and of secondary reactions on the anode surface, particularly in alkaline medium.

Fig. 1. Results of measuring steady-state electrode potentials of the main minerals of the Maleyevskoye pyrite-polymetal deposit at different pH values of medium (a) and a change in current density of chalcopyrite-sphalerite galvanocouple with time, mV/degree (b): pyrite: 1) +14; 2) –6,3; 3) –15; chalcopyrite: 4) –21; 5) –60; sphalerite: 6) –2,5; 7) with air purging; 8) without purging.

Electrochemical oxidation processes related to the work of microgalvanic elements, are rather widespread in nature in the formation of hypergenesis zones. Electrochemical processes and chemical oxidation processes are interrelated and mutually enhancing. Current strength of galvanocouples made of mineral electrodes (simulating natural aggregates), under conditions of active aeration contributing to chemical oxidation of mineral surface, is increased (for the case in Fig. 1, *b* by a factor of about 2). The generated electrochemical currents, in turn, intensify chemical oxidation of electrodes accompanied by

formation of secondary minerals (Fig. 2). It was established that the electrochemical properties (electrode potential) and the Seebeck coefficient depending on specific features of mineral crystal structure, the character of impurity atoms entry into crystal lattice of sulfides, are closely correlated [7].

Fig. 2. Result of work of microgalvanic elements formed by p-type pyrite (position1, light-yellow, relief) and n-type chalcopyrite (position 2, orange, oxidized) in the ore of the Rubtsovskoye deposit: bornite (position 3, brick-red), covellite (position 4, blue), chalcosine (position 5, crimson).

The fact that pyrites qualitatively prevail in polysulfide ores allows singling them out as a mineral which is most responsible for semiconductor properties of ores. From comparison of the composition of pyrites of metacolloidal and crystalline ores in Table 6 it follows that despite the identical collection, the concentration of impurity elements differs considerably, and dependence thermoEMF of pyrites on the content of individual elements in them (Fig. 3) permits a conclusion to be made on the impurity nature of iron sulfides conductivity. Hence it follows that there exists a certain relation between thermoelectric characteristics of pyrite matrices of ores and microsystems of carrier minerals comprised in them (sphalerite, chalcopyrite) with emulsion or microimpregnated inclusions of other minerals (pyrite, chalcopyrite, galenite).

Table 6

Content of the main elements-impurities in the pyrites of ores of the Nikolayevskoye deposit

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To characterize the thermoelectric properties of ores, P.S. Revyakin [8] proposed a term "the Seebeck effect" denoting the total thermoEMF value of minerals in the ore which is a resultant of this parameter with a simultaneous measurement of thermoEMF value of crystal grains composing the ores (including those with different conductivity type) and is proportional to the share and thermoEMF value of predominant-sign crystals.

Practical use of this parameter makes it possible not only to separate and trace different types of sulfide ores in the mine workings (Fig. 4, Table 7), but also to localize zones corresponding to different stages of deposit ore formation (Fig. 5).

Fig. 4. Results of measuring the Seebeck effect in the quarry of the Nikolayevskoye ore mine: М – crystalline copper-pyrite ores; МС – metacolloidal copper-zinc ores; Р – veinlets of barite-polymetal ores.

Table 7

The Seebeck effect in the ores of pyrite-polymetal deposits of Rudny Altai

Deposit,	Conductivity type, μ V/degree	
Natural types of ores	Prevalence of electron conductivity	prevalence of hole conductivity
Nikolayevskoye deposit		
Metacolloidal ores		98;510 275
Transient ores	$-258; -0.63$ -125	18.7; 420 110
Crystalline ores	$-520; -110$ -315	
Orlovskoye deposit		
Polymetal ores	$-480; -18$ -276	5;520 206
Copper-pyrite ores	$-590; -127$ -360	
Maleyevskoye deposit		
Polymetal ores	-510 ; -12.8 -260	34; 490 211
Copper-zinc ores	$-605; -208$ -418	
Rubtsovskoye deposit		
Polymetal ores	$-390; -23$ -186	11.8; 620 316
Note. In the numerator – the minimum and maximum values, respectively, in the denominator – the average value.		

Fig. 5. Schematic of thermoEMF versus crystallization temperature of pyrites (a) and schematic of through-tier zoning of the electrical properties of pyrites of pyrite-polymetal deposits (b). Areas: 1 – low-temperature barite-polymetal ores;

2, 3 – medium-temperature polymetal and copper-zinc ores, respectively;

4 – chlorite-quartz metasomatites of iron-magnesium metasomatism area;

5, 6 – relatively high-temperature pyrite and copper-pyrite ores, respectively;

 7 – ceriсite-quartz metasomatites of acid leaching zone. Areas of change in electrical properties:

1′ *– barite- and carbonate-polymetal veinlets with p-type pyrites;*

2′ *– chlorite metasomatites and quartzites with p-type pyrites;*

 3′ *– sericite-quartz metasomatites with n-type pyrites (external zone); 4*′ *– the same, internal zone;*

5′ *– granitoids. Sign "+" corresponds to positive thermoEMF values, sign "–" – to negative.*

From the represented data it is seen that the natural types of ores are characterized by different electrophysical properties. Such distribution is exemplified by the ores of the Nikolayevskoye deposit. According to electrophysical properties, in the ores of this deposit there are zones with prevalent hole conductivity, prevalent electron conductivity and mixed conductivity. Localization of contacting ore bunches with different conductivity type causes formation of natural thermoelectric elements.

The technological properties of studied ores have the following specific features:

– in combination, the natural microgalvanic and thermoelectric elements in potential-forming medium are the reason for ignition of sulfide ores in their natural occurrence and in ore stockpiles or dumps. Isolation in the wells and minings during different prospecting stages of ores with different electrophysical properties allows estimating their fire hazard [9]. It is established that if the potential of natural electric field formation is $500 \div 700$ mV, the fire hazard of the deposit is high;

– the presence of natural microgalvanic elements (aggregates) in the ores has a negative effect on flotation processes, due to which by the results of determination of electrophysical properties one can recognize the rebellious ores;

– electrochemical reactions occurring in operation of natural thermoelectric and microgalvanic elements, have a beneficial effect on hydrometallurgical ore dressing techniques, intensifying oxidation processes. Owing to this, as early as at the stage of studying the electrophysical properties, one can estimate the advisability of using a hydrometallurgical technique for ore dressing.

Conclusions

Geological formations, just as any natural bodies, tend to retention of equilibrium state. Any external exposures disturbing geosystem stability, initiate a response in the form of chemical and energy processes in crystal mass aimed at restoring the equilibrium.

Electrophysical properties of sulfide minerals belonging to semiconductor class due to peculiarities of material composition and structure are of considerable importance both in formation and life cycle of pyrite-polymetal and refractory pyrite and arseno-pyrite gold-bearing ore deposits. The zone structure of such deposits corresponds to thermobarogeochemical conditions of mineralization at each stage of ore body formation. With a change in the external conditions of stable existence of polysulfide ore deposit, getting its head into erosive truncation zone exposed to potentialforming medium (water, atmosphere air), the process of chemical oxidation of ore minerals is intensified by microgalvanocouples coming into operation (mineral aggregates with different conductivity type). The emerging electrochemical currents many times intensify the oxidation process, which raises essentially the temperature of ore body in oxidation zone. As a result, there is not only a reversal of temperature gradient direction (earlier determined by geothermal heating in the ore body fringe), but the gradient value itself is also considerably increased. A synergistic effect takes place which is manifested in the work of thermoelement formed by ore layers with different conductivity types. Currents generated thereby form an electrical field with a dipole structure activating the work of natural galvanocouples and intensifying mineral oxidation process. Such self-organization process goes on until there is full conversion of sulfide minerals contacting with potential-forming medium into secondary minerals and a new balance is established between the material and energy components of geological system.

Semiconductor properties of sulfides are the most important characteristic of pyrite-polymetal deposit ores. In combination with other geophysical methods of parameter estimation (electrode potentials, early stage of induced polarization), contact method of polarization curves, measurement of thermoelectric properties of ores and ore minerals yields information on the ontogeny, genesis of accumulation helpful in the search, exploration and estimation of explored deposits. On the other hand, thermoEMF measurements allow classifying the ores by technological types, predicting the history of ore treatment processes, in particular, flotation and hydrometallurgical ore dressing methods, estimating the degree of fire hazard of polysulfide deposits.

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