Metallic sulphide and sodium carbonate interacting processes

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Abstract
The article deals with a review of publications and patents on interacting mechanisms of sodium and potassium carbonate - hydroxide with nonferrous sulfides/iron in neutral and oxidizing medium. Nonferrous sulfide like lead sulfide is reduced to metal in inert atmosphere or in the presence of carbonaceous reducing agents, alkali metals form sodium and potassium sulfides. Soda and sulfate melting techniques were tested on an industrial scale but were not widely used.

Some technologies use smelting sulphidic materials in molten alkali with the delivery of oxygen containing gas. These technologies allow to recover sulfides of lead, copper, nickel and iron to metal at low temperatures from 340-350°C up to 600-700°C. Sulfides of these metals transit to sodium and potassium sulfates in the presence of oxygen. The given technologies are environmentally friendly due to no release of sulfur-containing gases.

The interaction of nonferrous and iron sulfides with sodium and potassium carbonate is little-studied. Patent 4,541,993 (USA) offers joint sulphatization roasting of sulphide ores and carbonate or bicarbonate of alkali metals for extracting non-ferrous (copper, nickel, cobalt and zinc).

Studies of the behavior of PbS, Cu₂S, Bi₂S₃, FeS₂ in molten salt of Na₂CO₃-NaCl showed that PbS when reacting with Na₂CO₃ forms PbO and the reaction of PbO and PbS forms lead. The research is aimed at analyzing thermodynamic systems MeS-O₂-Na₂CO₃; determining the temperature of initial reactions of sodium carbonate with sulfides of copper, lead, zinc and iron; studying the extent of Cu₂S desulfurization at adding sodium carbonate in the mix material and air inlet or delivery under the filter layer. The study included the use of sulfides and natural minerals produced by synthesis, the X-ray analysis of raw materials and products produced by the method of synthesis, chromatographic analysis of gases on carbon dioxide content.

The composition of exhausted gases was monitored during a continuous heating of a test charge at the heating rate 10 K/min. It enabled to reveal the initial stage of desulfurization of copper, iron, lead and zinc sulfides, possibly caused by the change of homogeneity field of the sulfide composition. At the known processes the oxidation order of simple non-ferrous sulphides proceeds as follows: FeS, ZnS, PbS, Cu₂S. This sequence changes in the presence of sodium carbonate and oxygen: Cu₂S (415-430°C), FeS₂ (490-515°C), FeS (530-545°C), PbS (545-560°C), ZnS (735-750°C).

At mix material roasting consisting of copper sulfide we used planning experiment methods. There were found partial dependences between the effect of temperature and duration of the experience on the desulfurization degree. They are presented in the form of straight line equations, isochor for desulfurization extent from 36.6 to 84.4% at temperatures 500-600°C.

The air flow rate and the flow rate of soda used in experiments were close to the theoretically necessary figures and when the degree sulphide conversion was reached, they had no significant effect. The dependence of these factors is described by the mean value.

The maximum desulfurization degree is achieved at a greater burning time and temperature. Leaching and thermodynamic analysis of a roasted product allowed to determine that oxide Cu₂O and
Chemistry of metals

Introduction
In 1953-1975 K.V. Sushkov’s research group [1] studied lead concentrates smelting in soda solution. Lead- sulfide concentrate was being treated in sintering machines with adding soda ash and coal to a mix material. The agglomerate was melted in a shaft furnace without adding fluxes that resulted in obtaining crude lead and melted slag. Also they offered a method of direct lead concentrate melting in ore-smelting furnaces without agglomeration [2] with adding caustic soda and carbon reducers into a mix material for recovering lead from sulphides under the following scheme:

\[
2\text{PbS} + 2\text{Na}_2\text{CO}_3 + \text{C} = 2\text{Pb} + 2\text{Na}_2\text{S} + 3\text{CO}_2
\]

V.A. Luginanov [3] used a soda melt method for processing lead and zinc-containing sulphate dusts of copper plants. See main reactions of sulfates reduction to lead:

\[
\begin{align*}
2\text{PbSO}_4 + \text{Na}_2\text{CO}_3 + 5\text{C} &= 2\text{Pb} + 2\text{Na}_2\text{S} + 3\text{CO}_2, \\
\text{Pb}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + 2\text{C} &= \text{Pb} + \text{Na}_2\text{SO}_4 + 3\text{CO}, \\
2\text{Pb}_2\text{SO}_4 + 2\text{Na}_2\text{SO}_4 + \text{C} &= 2\text{Pb} + 2\text{Na}_2\text{SO}_4 + 3\text{CO}_2
\end{align*}
\]

Reduction melting of lead-containing materials was carried out industrially by I.R.Polyvany’s research group [4].

Recent decades are characterized by extensive studies of melting sulphide concentrates with sodium and potassium salts and the development of lead, copper and nickel concentrate processing methods.

N.V. Khodov’s patent [5] proposes to recover lead by feeding lead-containing products and oxygen containing gases to the reaction zone of molten potassium hydroxide at a temperature of 600-700°C for producing lead bullion and a melt containing potassium hydroxide, potassium sulfate, potassium carbonate, zinc sulfide, copper, iron and gangue.

V.I. Maslov’s patent [6] proposes a method of complex processing polymetallic sulfides of raw heavy non-ferrous and precious metals by their separation melting in a deep bath furnace with adding into it a mixture of alkali metal salts and a carbonaceous reducer. The method results in production of crude metals, slag, slag-matte melts. The latter are being used as a flux for melting antimony that result in obtaining matte or cake further used in melting lead or precious metal raw materials.

V.A. Motovilova’s patent [7] proposes to process sulfide products in alkaline melt. This method differs by using in melt a mixture of sodium hydroxide NaOH and potassium hydroxide KOH, in a weight ratio of NaOH:KOH from 0.65 to 0.75. Using a mixture of alkali reduces a melting temperature from 400-600°C to 200°C. Melting pyrite concentrates in a melt produces disulfides of alkali metals in the form Na$_2$S$_2$ and K$_2$S$_2$ and iron in the form of hydroxide Fe(OH)$_3$, black in color.

S.P. Baksheev’s dissertation "Sulfide and oxygen compounds reduction to lead in alkaline media in respect to metal production from mineral and secondary raw materials", supervised by B.C. Chekushin [8] studied the basics of sulfide and oxygen compounds reduction to lead in molten alkali and describes environmentally and economically friendly technology developed for recycling mineral and secondary lead raw materials.

V.S. Chekushin’s patent [9] proposes to produce crude lead by treating concentrates by treating them with an alkali and further melting. Cakes together with alkaline are being charged into the furnace with the molten return slag and stirred intensively. Cakes made of concentrates and alkali are prepared at a temperature of 220-250°C after wet charge preparation of a concentrate with 15-50% NaOH of the total weight of concentrate. This method reduces the process time, has a minimal impact on the environment and provides high lead recovery efficiency.

N.V. Oleinikova’s article [10-12] proposes to recover sulfides in alkaline melt by electrochemical processing that involves the electrode pair Mez$^+$ and S$^2_-$ that interacts under internal electrolysis conditions realized in alkali melt and ensuring the recycling of elemental sulfur produced by chemical reactions ". The team studied the influence of a set of factors on lead metallization and confirmed chemism of elemental sulfur recovery associated with its disproportionation and S$^2_-$ and SO$_4^{2-}$-accumulation, with a possible polysulfide sulfur formation. It also studied the mechanism of Pb recovery from galenites of different lead concentrates in alkaline media.

CuO were the main products of copper sulfide burning in the presence of sodium carbonate and delivery of oxygen-containing gas.

Key words: NON-FERROUS METALLIC SULPHIDES, PYRITE, MARTITE, CHALCOCITE, GALENITE, SPHALERITE, SODIUM SULFATE, SODIUM CARBONATE, ROASTING, SULPHATIZATION, OXIDATION, LEACHING
V.S. Chekushin’s patent [13] proposes to recover copper from sulfide products in molten alkali with stirring it intensively by a mechanical paddle. The process was carried out at a temperature of 450-480°C, 30-40 min. and oxygen barbotage. The oxygen flow rate was 350-375% of the total weight of sulfur present in the initial sulphide product. The method enables to achieve high speed of copper plating without material concretions.

V.S. Chekushin’s patent [14] offers to process nickel containing sulfide materials for nickel reduction by using caustic soda, technical oxygen and stirring. Nickel reduction is carried out at a temperature of 700 ± 10°C. Industrial oxygen consumption is 1.5-1.7% of the total weight of the product, 10-15 min. rubbing/stirring. Then by magnetic separation method we separate concomitant copper from melt at a temperature of 340-350°C. Nickel precipitates concentrated on magnetic cores and containing alkaline melt are being subject to watering from caustic soda, sodium sulfate, nonmagnetic copper particulates and phase separation through centrifugation. Magnetic nickel precipitates after magnetic rod demagnetization are being floated out thus obtaining decoppered nickel.

The article [15] experimentally confirms the possibility of direct recovery of nickel from its sulphides (Heazlewoodite, pentlandite, disulfide) by means of its intrinsic sulfide sulfur in sodium hydroxide melt; the temperature interval 550-700°C, metallization efficiency reaches 95-98%. The chemistry of reactions varies depending on contact duration between phases (8-12 min.). In alkaline melt there are accumulated sodium polysulfides able to disproportionate and form neutral sulphide sulfur. The process of sulphide reduction to nickel is limited by pore-diffusion kinetics.

D.A. Norgrga’s patent [16] proposes to recover some nonferrous metals (copper, nickel, cobalt and zinc) from sulfide ore by co-firing with a carbonate or bicarbonate of alkali metals, eg, with sodium carbonate added to mix material for obtaining sulphatization reaction. For enriching ore containing copper, nickel, cobalt or zinc sulfide there is used a flotation method. The resulting concentrate mixed with carbonate or bicarbonate is being calcined. The roasted product is being mixed with water to separate soluble sulphates of metals from iron compounds and other solid residues. Sulfate solution is being filtered for removing particulate matter and non-ferrous metals recovered by precipitation or by internal electrolysis. Consumption of alkali metal carbonate is 10 to 20% from the total weight of a roasted product, the firing temperature from 550°-650°C, firing time 2-4 hours.

Longgang Ye, Chaobo Tang’s paper [17], School of Metallurgy and Environment, CSU, China, studied experiments on behavior of sulfides during melting done for developing a method of smelting antimony at low temperatures. They carried a thermodynamic study of behavior of sulphides PbS, CuS, Bi₂S₃, FeS₂ and in molten salt Na₂CO₃-NaCl by using XRD and TG-DSC techniques. The results showed that PbS when reacting with Na₂CO₃ forms PbO and lead is produced by interaction of PbO and PbS. The decomposition reaction of Bi₂S₃ starts after temperature 873 K, sulfide also interreacts with Na₂CO₃ forming Na₂S and Bi₂O₃, and easy production of NaBiS₂. Cu₂S is stable and its treatment in molten salts up to a temperature of 1173 K causes no changes in its microstructure. FeS is being produced by decomposition of FeS₂ and a steady NaFeS₂ as a result of Fe and Na₂S interaction. Therefore, in the process of melting lead and bismuth transform into crude antimony.

Conclusions

During roasting and smelting putting alkali metal salts to mix material containing ferrous metal sulfides can "bind" sulfur to sulfides or bind sodium and potassium sulfates. A roasted product (calcine) obtained after roasting is being subject to leaching. Sodium and potassium sulfates after leaching can be sent on regeneration of alkali metal salts returned for recycling as well as for obtaining the necessary amount of sulfuric acid. Most of publications regard chlorides and hydroxides of sodium and potassium as reagents, but there are few research and publications on sulfide oxidation by atmospheric oxygen and input of sodium carbonate into mix material.

Goal of research

The analysis of thermodynamic systems MeS-O₂-Na₂CO₃: determination of the initial reaction temperature of sodium carbonate with iron and nonferrous metal sulfides; study study of desulfurization efficiency of copper sulfide Cu₂S on addition of sodium carbonate into mix material and delivery of air to the filter bed.

Research technique

Starting and raw materials: copper sulfide - Cu₂S and iron sulphide FeS of grade B (indicates the presence of rare earth metals) – The Ural Plant of chemicals; lead sulfide PbS prepared from components in a sealed tube; natural sulphides - galena PbS from Rodnikov deposits, sphalerite ZnS from Shalkya deposit (Kazakhstan) and pyrite FeS₂.

The composition of elements found in test samples was determined by X-ray technique, instrument "SPARK-1."
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The content of CO₂ in gases was determined by a chromatograph "Gazohrom - 3101". Control and regulation of temperature in nickel-chrom heater furnace was carried out by thermocouple PP-1 and potentiometer SH4501. Reaction zone temperature was measured with an additional thermocouple and digital device DT-838. A test charge material was weighed on electronic scales VLT-510-P (capto).

Results and discussion

Polymetallic sulphide concentrates contain: FeS₂ - pyrite, FeS - martite, CuFeS₂ - chalcopyrite, CuS - covellite, Cu₂S - chalcocite, ZnS - sphalerite (wurtzite), PbS – galena and sulphides of related small and rare metals. Higher sulphides dissociate to the lower sulphides and sulfur at temperatures of 350°C or more when heated. According to research literature, the start of decomposition of higher sulphides proceeds under atmospheric pressure and at the following temperatures: covellite CuS - 673 K; chalcopyrite CuFeS₂ - 823 K; Pyrite FeS₂ - 852 K; nickeline NiS - 1073 K. R.A.Isakova’s research data [18] show that lower sulfides of iron and nonferrous metals dissociate appreciably only at temperatures above 1373 K when heated and consequently they do not decompose at heating. The vapor pressure and pressure metal sulfides dissociation that are studied in this paper are calculated by approximation equations [18], which allows to arrange them in pressure descending order (Table 1).

Table 1. Metal sulfides vapor pressure and pressure of sulfur vapor over sulfide

<table>
<thead>
<tr>
<th>#</th>
<th>Sulfide</th>
<th>Pₘₑₙ, Pa</th>
<th>#</th>
<th>Sulfide</th>
<th>Pₛₛ, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PbS</td>
<td>133.3 * 10^-0.99</td>
<td>1</td>
<td>PbS</td>
<td>133.3 * 10^-4.799</td>
</tr>
<tr>
<td>2</td>
<td>ZnS</td>
<td>133.3 * 10^-2.41</td>
<td>2</td>
<td>FeS</td>
<td>133.3 * 10^-6.445</td>
</tr>
<tr>
<td>3</td>
<td>Cu₂S</td>
<td>133.3 * 10^-4.97</td>
<td>3</td>
<td>The Cu₂S</td>
<td>133.3 * 10^-7.005</td>
</tr>
</tbody>
</table>

To determine the possibility of caustic soda NaOH and Na₂CO₃ in processing sulfide materials there were calculated changes of enthalpy and Gibbs energy in systems MeS - NaOH, MeS - Na₂CO₃, the temperature interval 298-2100 K taking into account polymorphic and aggregate transformations of substances.

Determination of changes of Gibbs energy in neutral atmosphere for systems Cu₂S - NaOH

\[
\begin{align*}
\text{Cu}_2\text{S} + 2\text{NaOH} &= \text{Na}_2\text{S} + \text{Cu}_2\text{O} + \text{H}_2\text{O} \\
\delta G_{298} &= 114,475 \text{ kJ}. & (1) \\
\text{Cu}_2\text{S} + 2\text{NaOH} &= \text{Na}_2\text{S} + \text{Cu(OH)}_2 \\
\delta G_{298} &= 131,885 \text{ kJ}. & (2) \\
3\text{Cu}_2\text{S} + 4\text{NaOH} &= 2\text{Na}_2\text{S} + 6\text{Cu} + 2\text{H}_2\text{O} + \text{SO}_2 \\
\delta G_{298} &= 310,784 \text{ kJ}. & (3) \\
4\text{Cu}_2\text{S} + 8\text{NaOH} &= 3\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4 + 8\text{Cu} + 4\text{H}_2\text{O} \\
\delta G_{298} &= 99,583 \text{ kJ}. & (4)
\end{align*}
\]

Positive values of Gibbs energy change for reactions (1-4) say about the impossibility of their occurrence.

\[
\begin{align*}
\text{Cu}_2\text{S} + 2\text{NaOH} + 1,5 \text{O}_2 &= \text{Na}_2\text{SO}_4 + 2\text{Cu} + \text{H}_2\text{O} \\
\delta G_{298} &= -653,099 \text{ kJ}. & (5) \\
\text{Cu}_2\text{S} + 2\text{NaOH} + 2 \text{O}_2 &= \text{Na}_2\text{SO}_4 + \text{Cu}_2\text{O} + \text{H}_2\text{O} \\
\delta G_{298} &= -800,954 \text{ kJ}. & (6)
\end{align*}
\]

Only reactions (5,6) of copper sulfide with caustic soda in the presence of atmospheric oxygen are thermodynamically probable. Systems MeS - Na₂CO₃: Reactions of producing metal oxide and sodium sulfide have positive Gibbs energy changes in a wide temperature range. The nature of these changes speaks about the impossibility of spontaneous process occurrences subject to given circumstances, see the following schemes:

\[
\begin{align*}
\text{Cu}_2\text{S} + \text{Na}_2\text{CO}_3 &= \text{Cu}_2\text{O} + \text{Na}_2\text{S} + \text{CO}_2 \\
\delta G_{298} &= 237,489 \text{ kJ}. & (7) \\
\text{PbS} + \text{Na}_2\text{CO}_3 &= \text{PbO} + \text{Na}_2\text{S} + \text{CO}_2 \\
\delta G_{298} &= 208,248 \text{ kJ}. & (8) \\
\text{ZnS} + \text{Na}_2\text{CO}_3 &= \text{ZnO} + \text{Na}_2\text{S} + \text{CO}_2 \\
\delta G_{298} &= 177,259 \text{ kJ}. & (9) \\
\text{FeS} + \text{Na}_2\text{CO}_3 &= \text{FeO} + \text{Na}_2\text{S} + \text{CO}_2 \\
\delta G_{298} &= 155,355 \text{ kJ}. & (10)
\end{align*}
\]
Metals carbonatation in the following reactions is also thermodynamically impossible:

\[
\begin{align*}
\text{Cu}_2S + \text{Na}_2\text{CO}_3 &= \text{Cu} + \text{CuCO}_3 + \text{Na}_2S, \quad \Delta G(298) = 260,596 \text{ kJ} \quad (11) \\
\text{CuS} + \text{Na}_2\text{CO}_3 &= \text{CuCO}_3 + \text{Na}_2S, \quad \Delta G(298) = 230,991 \text{ kJ} \quad (12) \\
\text{PbS} + \text{Na}_2\text{CO}_3 &= \text{PbCO}_3 + \text{Na}_2S, \quad \Delta G(298) = 165,851 \text{ kJ} \quad (13) \\
\text{ZnS} + \text{Na}_2\text{CO}_3 &= \text{ZnCO}_3 + \text{Na}_2S, \quad \Delta G(298) = 160,494 \text{ kJ} \quad (14) \\
\text{FeS} + \text{Na}_2\text{CO}_3 &= \text{FeCO}_3 + \text{Na}_2S, \quad \Delta G(298) = 128,747 \text{ kJ} \quad (15)
\end{align*}
\]

Gibbs energy changes in sodium sulfide, oxides and carbonates of metals reactions under neutral atmosphere are at positive at roasting and smelting temperatures used in non-ferrous metallurgy (700-1300°C). Consequently, this way sulfides - sodium carbonate reactions in inert atmosphere is thermodynamically impossible. As for systems where the starting materials are metal oxides and carbonates, iron and nonferrous metal sulfidation reactions on addition of sodium sulphide are thermodynamically possible. It is documented by the use of sodium sulfide in flotation of ores containing metal oxides.

**Systems MeS-O₂-Na₂CO₃**: Sulfur and lower sulfides exothermic oxidation reactions proceed in oxidizing atmosphere. These reactions are well studied. They are the basis of sulphating and oxidizing roasting and smelting technology for sulphide concentrates, as well as for a technology of autogenous smelting of sulfide raw materials. Sulfides of iron and nonferrous metals can be oxidized at temperatures of 450-600°C and form sulfates, they are oxidized to oxides at temperatures of 700-1000°C. Oxidation reactions at more high temperatures cause the interaction of generated oxides and sulfides and the presence of metals in final products. On such reactions there is based the obtaining of blister copper in a converter and of lead by method of roast-reaction smelting.

\[
\begin{align*}
\text{Cu}_2S + 1,5 \text{O}_2 &= 2 \text{Cu} + \text{SO}_2, \quad \Delta G_{298} = -213,876 \text{ kJ}. \quad (17) \\
\text{Cu}_2S + \text{O}_2 &= \text{Cu}_2\text{O} + \text{SO}_2, \quad \Delta G_{298} = -361,731 \text{ kJ}. \quad (18)
\end{align*}
\]

For comparison, see. thermodynamic analysis of MeS-Na₂CO₃-O₂ systems:

\[
\begin{align*}
\text{Cu}_2S + \text{Na}_2\text{CO}_3 + 1,5 \text{O}_2 &= 2\text{Cu} + \text{Na}_2\text{SO}_4 + \text{CO}_2, \quad \Delta G_{298} = -530,084 \text{ kJ}. \quad (19) \\
\text{Cu}_2S + \text{Na}_2\text{CO}_3 + 2\text{O}_2 &= \text{Cu}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{CO}_2, \quad \Delta G_{298} = -677,939 \text{ kJ}. \quad (20) \\
\text{CuS} + \text{Na}_2\text{CO}_3 + 2\text{O}_2 &= \text{CuO} + \text{Na}_2\text{SO}_4 + \text{CO}_2, \quad \Delta G_{298} = -687,779 \text{ kJ}. \quad (21)
\end{align*}
\]

Oxygen and sodium carbonate reactions have large negative values of Gibbs energy in the whole temperature interval. It speaks for a high thermodynamic probability of reactions with the yield of copper metal and metal oxide in reaction products. In the case of using sodium carbonate all sulfur of sulphide concentrates can be linked into solid sodium sulfate, which can be separated from reaction products by water leaching.

The overall comprehension of chemical reactions in a complex system that includes the most common metal sulfides, sodium carbonate and oxygen see in see in sulfides diagram 1.

Reactions are arranged downward in ascending order of thermodynamic probability of reactions proceeding under these conditions and their conversion. Comparison of calculated data by programmes of NASA, HSC Chemistry, Ivtrantermo for Windows provides values that slightly differ but at large the order of reactions stays unaltered.

For non-ferrous metal sulfides the reaction of metal oxide formation in the product is more likely. The development of metal is also possible at sulfur retention into sodium sulphate Na₂SO₄ and precipitation of carbon dioxide gas CO₂.

Magnetite Fe₃O₄, hematite Fe₂O₃, iron oxide, FeO and metallic iron Fe are the most likely products of iron sulfides reaction with sodium carbonate in oxidizing atmosphere.

**Assessment of reactions initiation temperature by testing gases for CO₂**: a method of determining the sodium carbonate sulfation efficiency and consequently metal sulfides desulfurization efficiency was selected adjusted for thermodynamics and by gas analysis for carbon dioxide. In this given case it is difficult to use thermographic techniques, in particular the DTA method, in view of the necessity to deliver gaseous oxidizer and its effect on heat balance in derivatograph cells.

The experiments were carried out in precoat regime. In order to ensure oxygen delivery to precoat...
filter material, we used a reactor made of alundum crucible (see fig.2). Air blast and a sulfide test portion were fed to the crucible through a two-channel alundum tube tightly fixed to the end-opening surface of the crucible. On top end-openings were covered with an alundum disk. Such air feeding ensures a uniform supply of oxygen to sulphide particles that is documented by the throughout discoloring of the roasted product.

Preliminary experiments with mix material heating containing sulfide and sodium carbonate in a temperature range of 25-750°C confirms the absence of $\text{CO}_2$ separation due to sodium carbonate decomposition or due to catalytic effect of sulfides. Carbon dioxide starts to release from a test portion only at air injection. The gas flow rate was adjusted by rotameter calibrated against foam flowmeter.

In the first series of experiments we heated a sulfide test portion in the a sealed alundum reactor, furnace heating rate being 10 K/min. Test results of final gases for $\text{CO}_2$, see Fig.3.
Fig. 3 shows a distinctive pattern of changes for carbon dioxide in gases:

- The first small peak of CO$_2$ separation is a feature of all sulfides, that is apparently connected with the release of elemental sulfur due to the change in composition in the field of homogeneity of sulfide.
- The onset of sulfide oxidation of the metal edge of homogeneity area is characterized by sharp increase in desulfurization rate and consequently the transformation of sodium carbonate into sulfate that is accompanied by a rapid increase carbon dioxide concentration in off-gases.
- Sharp increase in CO$_2$ concentration is a sign of the onset of metal sulfide reaction with sodium carbonate.
- In known processes the order of the onset of oxidation processes of simple non-ferrous metal sulphides has the following sequence: FeS, ZnS, PbS, Cu$_2$S. The order of sulphide oxidation in the presence of sodium carbonate and atmospheric oxygen varies considerably: Cu$_2$S (415-430°C), FeS$_2$ (490-515°C), FeS (530-545°C), PbS (545-560°C), ZnS (735-750°C).

The order of sulphides oxidation obtained in experiments in the presence of sodium carbonate and atmospheric oxygen does not correlate with the vapor pressure of sulfides and dissociation elasticity. This fact can not be explained by sulfides dissociation or by the transport of sulfide molecules through gas phase.

**Copper sulfide Cu$_2$S roasting with sodium carbonate.** Metallurgy of nonferrous metals characterizes copper sulfide like the most rigid compound that oxidizes less and more difficult compared with the sulfides of iron, zinc and lead. However the thermodynamic analysis data and experiments on initial reaction temperature determination showed that chalcosine in oxidizing atmosphere and on addition of sodium carbonate should be oxidized at relatively low temperatures of 375-400°C. A probabilistic-deterministic method of planning experiments was used in conducting oxidative roasting of a sulfide Cu$_2$S test portion weighing 5 grams and carbonate Na$_2$CO$_3$. Sulfide desulfurization efficiency values see in Table 2.

Table 2. Experiment conditions and results

<table>
<thead>
<tr>
<th>Test №</th>
<th>Temperature, °C</th>
<th>Soda consumption, gram</th>
<th>Air flow, L/h</th>
<th>Desulfurization efficiency/degree Y, %</th>
<th>Insoluble acid residue yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600,00</td>
<td>2.20</td>
<td>6.90</td>
<td>89.4</td>
<td>25.18</td>
</tr>
<tr>
<td>2</td>
<td>600,00</td>
<td>2.00</td>
<td>5.75</td>
<td>70.5</td>
<td>51.97</td>
</tr>
<tr>
<td>3</td>
<td>600,00</td>
<td>1.80</td>
<td>4.60</td>
<td>48.2</td>
<td>65.46</td>
</tr>
<tr>
<td>4</td>
<td>550,00</td>
<td>2.20</td>
<td>5.75</td>
<td>45.2</td>
<td>62.72</td>
</tr>
<tr>
<td>5</td>
<td>550,00</td>
<td>2.00</td>
<td>4.60</td>
<td>72.38</td>
<td>40.00</td>
</tr>
<tr>
<td>6</td>
<td>550,00</td>
<td>1.80</td>
<td>6.90</td>
<td>67.75</td>
<td>58.82</td>
</tr>
<tr>
<td>7</td>
<td>500,00</td>
<td>2.20</td>
<td>5.75</td>
<td>36.6</td>
<td>61.59</td>
</tr>
<tr>
<td>8</td>
<td>500,00</td>
<td>2.00</td>
<td>4.60</td>
<td>68.6</td>
<td>53.07</td>
</tr>
<tr>
<td>9</td>
<td>500,00</td>
<td>1.80</td>
<td>6.90</td>
<td>50.54</td>
<td>43.30</td>
</tr>
</tbody>
</table>

Copper sulfide desulfurization degree was measured by the CO$_2$ content and the volume of final gases from the reactor. The roasted product leached in water and measured the weight of residue. Following that we leached the residue in sulfuric acid solution with a concentration of 100g per liter and determined the weighed of residue obtained. At each stage, the copper content in solid residue was determined by X-ray method.

Copper sulfide desulfurization efficiency degree is equal to Na$_2$CO$_3$ decarbonization degree and also corresponds to sulfation degree that is associated with the formation of Na$_2$SO$_4$. Data processing results, see in Table 3.

<table>
<thead>
<tr>
<th>#</th>
<th>Impact factor factor</th>
<th>Types of partial dependency</th>
<th>Equation coefficient, dispersion equation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature, °C</td>
<td>$Y_1 = A_1 + B \times X_1$</td>
<td>$A_1 = -34,978$; $D_{A_1} = 1,722$; $D_{B_1} = 0.002$</td>
</tr>
<tr>
<td>2</td>
<td>Soda consumption, gram</td>
<td>$Y_2 = 61,019$</td>
<td>Average of test results</td>
</tr>
</tbody>
</table>
So we have made Protodiakonov’s equation that describes experimental data and the value of multiple correlation coefficient: \( Y_{Pr} = 0.016 Y_1 Y_2 \); \( R = 0.973 \).

Protodiakonov equation chosen as index is given by

\[
Y_{exp} = \exp[-0.594(Y_{Pr})^{0.442}];
\]

Correlation coefficient \( R = 0.66 \); significance level \( TR = 2.321 \).

Processing data showed that the conversion of substances under assumed experiment conditions ranged from 36.6 to 89.4%, soda and air oxygen consumption were sufficient for the reaction. The temperature and experiment time had a directly proportional effect on increase of conversion. Leaching of the roasted product enabled to transfer fully into solution the soda residue and salt cake formed during reactions. Acid leaching of a roasted product without oxygen aeration provides a transfer of cupric oxide CuO into solution. After acid leach the remainder contains cuprous oxide \( \text{Cu}_2\text{O} \) of rose color. Yield of insoluble residue is 25.18-65.46% from the weight of initial test portion of sulfide.

**Conclusion**

The abovementioned technologies offer to process sulfide materials in molten alkali media (KOH, NaOH), where non-ferrous metals and iron are selected in the form of dispersed particles hard separable from melts. Low melting lead is separated in the form of liquid phase only when processing rich lead containing concentrates. Using a mix product melt technology for polymetallic concentrates containing the approximately equal amount of copper, zinc, lead and iron is not reasonable due to complex metal alloys, oxides, silicates, sulfates potential.

It is advisable that the temperature for firing collective concentrate with soda ash be higher of higher sulphides dissociation temperature i.e. it should be more than 450°C. At this the firing temperature should correspond to the firing temperature that is sufficient for providing intense lower sulphides oxidation reaction (over 600°C) and be below the melting point for \( \text{Na}_2\text{CO}_3 \) (852°C) and for \( \text{Na}_2\text{SO}_4 \) (883°C).

Firing temperature can be selected in the range of 600-750°C due to exothermcity of sulphides oxidation reaction and local temperatures rise potential in the reaction zone on the surface of particles.