N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224-5278
Volume 1, Number 427 (2018), 74 – 78

A. Bayeshov, A. Konurbayev, U. Abduvaliyeva,
N. Sarsenbayev, A. Makhanbetov, D. Abizhanova

Institute of Fuel, Catalysis and Electrochemistry named after D. V. Sokolsky, Almaty, Kazakhstan.
E-mail: bayeshov@mail.ru, abibulla.kon@mail.ru, abdumida14@gmail.com, nurjan_s_b@mail.ru, diko77781@mail.ru

PRODUCTION OF CALCIUM SULPHIDE WITH USING ELECTROPRODUCTIVE COMPOSITE SULFUR-GRAPHITE ELECTRODE BY MEANS OF ELECTROCHEMICAL APPROACH

Abstract. This article provides the investigation results of the electrochemical process of calcium sulphide production. For this purpose, an electrically conductive composite sulphur-graphite electrode specially designed by authors was used. Sulphur and graphite are combined in this electrode in a proportion of 50:50. Electrochemical synthesis of calcium sulphide was carried out by stationary electrolysis in an electrolytic tank with separated electrode spaces. In order to separate the electrode spaces of the electrolytic tank, a cation-exchange membrane MK-40 was used. There is an influence of some parameters on the current yield of formation of sulphide ions. They were studied. These parameters include the current density, the concentration of sodium hydroxide and the duration of electrolysis. It is established that an increase in these parameters leads to an increase in the value of the current yield of formation of sulphide ions. It is shown that sulphur in the sulphur-graphite electrode actively reacts with calcium ions to form calcium sulphide. The maximum value of the current yield of calcium sulphide formation, produced by the electrochemical method, is 90%. The results of x-ray phase analysis and infrared spectroscopy indicate the formation of calcium sulphide. The electrochemical method for synthesis of calcium sulphide proposed by us is simple and economically advantageous.

Key words: electrochemistry, sulphur, graphite, composite electrode, calcium sulphide, proportion, current efficiency, membrane, current lead, synthesis.

The need for sulphur-containing compounds, such as sulphides, polysulphides, thiosulphates, sulphites, alkali metal sulphates, etc., widely used in the chemical, petrochemical, tanning, metallurgical and other industries is increasing every year [1-6]. To meet the demand of industries, it is necessary to establish the domestic production of salts, in particular sulphides, based on sulphur generated by technology using simple resource-saving technologies [7-10]. In this regard, the creation of highly efficient technologies for the synthesis of sulphur-containing multi-purpose products is an important task, and its solution gives significant ecological and economic effect.

The electrochemical method of producing calcium hydrosulphide is simple and economically advantageous and is required in the branches of the national economy. For example, calcium sulphide is widely used in the ore-dressing treatment of non-ferrous metal ores as a sulphidizer. The approximate sodium sulphide consumption, depending on the degree of ores oxidation, ranges from 10 to 600 g/t of oxidized copper ore. One of the advantages of using calcium sulphide is its improved organoleptic characteristic [11-20]. Calcium sulphide is odorless, which has a positive effect on the organization of occupational safety and health.

Work objective. The investigation is concerned with the creation of an electrochemical technology for the preparation of calcium sulphide solution (hydrosulfide) by means of an electrically conductive composite sulphur-graphite electrode with an established percentage of sulphur and graphite (ratio 50:50) in aqueous solutions of calcium chloride in membrane electrolyzers.

Research methods. For calcium sulphide production, the stationary electrolysis in the electrolyser with electrode spaces separated by cation-exchange membrane-MK 40 was used. To provide electrolysis, an electrically conductive composite sulphur-graphite electrode with a ratio S and C of 50:50 is made. Potentiometric method for determining the concentration of sulphide ions was carried out on an ionometer И-160 МИ, and a current-voltage method was performed on fluorat - 02-5M. The products obtained are identified by X-ray diffraction and infrared spectroscopy.

Main results. The effect of the current density in a graphite current lead on the CY of calcium polysulphide ions formation is studied. The results of the synthesis of calcium sulphides by the method of stationary electrolysis in the electrolyzer with electrode spaces separated by cathionite membrane (MK-40) are shown in table 1.

Table 1 – Influence of current density in a graphite current lead on the current yield of polysulfide ions formation

i, A/m^2	50	75	100	125	150
CY, %	35.0	45.0	65.0	85.5	86.0
Note: τ = 0,5 hour, electrolyte mixture: 1,0M $CaCl_2$, t = 25 °C.					

As we can seen from table 1, an increase in the current density leads to an increase in the current yield of polysulphide ions formation. The maximum values of the current output are set in the current density range from 110 to 150 A/m2.

We have investigated the effect of calcium chloride concentration and the duration of electrolysis on the current yield of polysulfide ion formation. As has been already noted above, the concentration of sulphide ions was determined by potentiometric and voltammetric methods. When increasing the concentration of calcium chloride in the range from 0.25 to 1.0 M, an increase in the current yield of polysulfide ions formation, respectively, from 30.0 to 98%, a further increase in the concentration up to 2.0 M does not lead to a significant change of current output (table 2).

Table 2 – Effect on the current yield of sulphide ions formation in sulphur-graphite lump electrode depending on the concentration of sodium hydroxide

C, M	0.25	0.5	1.0	1.5	2.0
CY, %	29.1	64.7	90.0	90.1	90.0
Note: i = 100 A/m^2, t = 25 °C, τ = 0,5 h.					

The determination of the maximum value and inhibition of the current output growth is explained by the achievement of high values of the electrical conductivity of the solution and saturation of the double electrical layer of the electrode surface by polysulphide ions with cathodically reducing sulphur and appearance of the diffusion limitation of the withdrawal from the surface of the reaction product. The above explanation also corresponds to the regularities on the influence of the electrolysis duration on the formation of hydrosulphide ions (table 3).

Table 3 – Influence of electrolysis duration on the current yield of sulphide ions formation

τ, hours	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0
CY, %	13.6	25.0	38.8	48.1	55.0	70.0	71.5	72.5
Note: i = 100 A/m^2, t = 25 °C.								

The electrolysis time interval from 0.25 to 1.5 hours favourably affects the current yield of polysulphide ions formation from the composite sulphur-graphite electrode, and a further increase in time in the interval of 1.5-2.0 hours results in a slight increase in the yield value the current of polysulphide formation. Such a slowing down of the current output (insignificant growth) is explained by the fact that when the electrode is continuously polarized from the S:C composition (50% -50%), the sulphur is selectively etched, thus the sulphur content decreases and the surface is saturated with graphite, which in turn, leads to an increase in the fraction of the hydrogen evolution reaction.

The first experiments showed that sulphur in the sulphur-graphite electrode actively reacts with calcium ions to form calcium sulphide, and the yellow colour of the solution indicates the presence of polysulphide ions in the solution.

$$S^0 + 2e = S^{-2} \quad (1)$$

$$Ca^{+2} + S^{-2} = CaS \quad (2)$$

$$nS^0 + S^{-2} = S_n^{-2} \quad (3)$$

$$Ca^{+2} + S_n^{-2} = CaS_n \quad (4)$$

The formation of polysulphide ions can proceed in the following directions, sulphur receives from the graphite two electrons becoming a negatively charged ion and immediately combines with the calcium cation. At the interface between the electrolyte-electrode (cathode) phases, a layer of sulphide ions of high concentration is formed, which is a good solvent of elemental sulphur, form polysulphides.

Figures 1 and 2 show experimental data obtained by X-ray diffraction analysis and infrared spectroscopy of the produced electrolysis product.

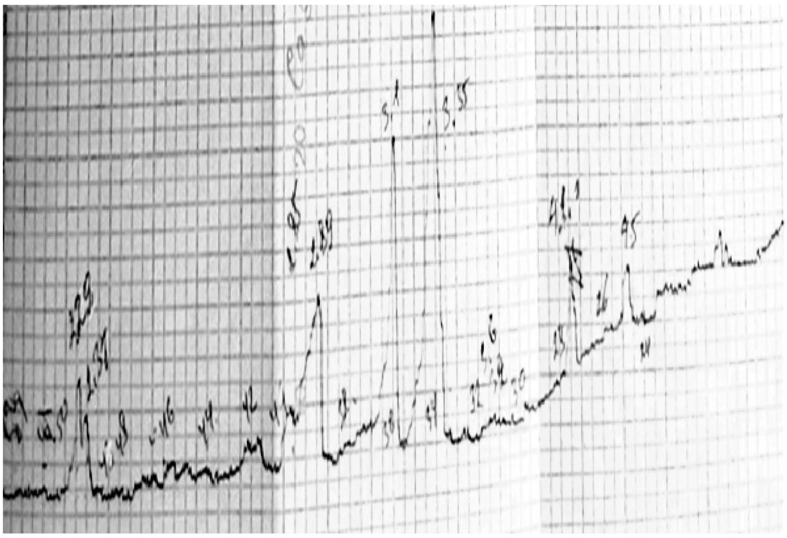

Figure 1 – X-ray pattern of calcium sulphide

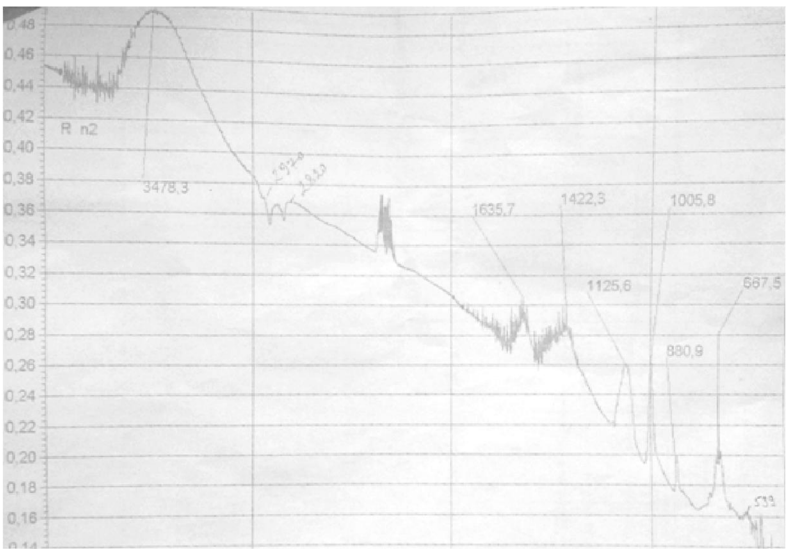

Figure 2 – Diagram of IR spectroscopy of hydrosulphide and calcium sulphide

Data of X-ray phase reflections from the card file (ASTM 8-464) (2.85x 3.017-1642) show the formation of calcium sulphide.

The explanation of the obtained IR spectroscopy diagrams also confirms the formation of calcium sulphide. This method also shows the presence of electrosynthesis in the product, in addition to calcium sulphide and calcium hydrosulfide.

Conclusions. Thus, in aqueous solutions of calcium chloride, the possibility of obtaining a solution of calcium sulphide (hydrosulphide) by means of an electrically conductive composite sulphur-graphite electrode with an established percentage of sulphur and graphite (ratio 50:50) is shown. It is determined that at the interface between the electrolyte-electrode (cathode) phases, a layer of sulphide ions of high concentration is formed, which is a good solvent of elemental sulphur, form polysulphides.

REFERENCES

[1] Kazankin O.N., Markovskiy L.YA. Neorganicheskiyelyuminofory. L.: Khimiya, 1975. 192 p.

[2] Gurvich A. M. Vvedeniye v fizicheskuyukhimiyukristallofosforov. M.: Vysshayashkola, 1971. 336 p.

[3] Garlick G.F.J. Mason D.E. Electron traps and infrared stimulation of phosphors // J. Electro-chem. Soc. 1949. Vol. 96. P. 90.

[4] Lehmann W. Ryan, F.M., Fast cathodoluminescent calcium sulfide phosphors // J. Electro-chem. Soc. 1972. Vol. 119. P. 275.

[5] Gorfinkel B.I., Abalduyev B.V., Medvedev R.S., Loginov A.P. Nizkovol'tnyye katodolyuminestsentnyye indikatory. M.: Radio isvyaz, 1983. 112 p.

[6] Lehmann W. Optimum efficiency of cathodoluminescence of inorganic phosphors // J. Electro-chem. Soc. 1971. Vol. 118. P. 1164.

[7] Grinvud N.N., Ernsho A. Khimiyaelementov.V 2-kh tomakh. M.: Binom, 2008. 1267 p.

[8] Dongdong Jia. Enhancement of Long-Persistence by Ce Co-Doping in CaS:Eu2+,Tm3+ Red Phosphor // Journal of The Electrochemical Sosiety. 2006. Vol. 153. P. 198-201.

[9] Wu J., Newman D., Viney I. Excitation-energy transfer in infrared – stimulableCaS doubly doped with Eu and Sm // Applied Physics B Lasers and optics. 2004. Vol. 79. P. 239-243.

[10] Avtorskoye svidetel'stvo SSSR № 34666, kl.22 f, 15. 1934 g.

[11] Chongfeng Guoa, Dexiu Huanga, Qiang Sub. Methods to improve the fluorescence intensity of CaS:Eu2+ red-emitting phosphor for white LED // Materials Science and Engineering B. 2006. Vol. 130. P. 189-193. 144

[12] Chongfeng Guo, Benli Chu, Mingmei Wu, Qiang Su. Oxide coating for alkaline earth sulfide based phosphor // Journal of Luminescence. 2003. Vol. 105. P. 121-126.

[13] Chongfeng Guo, Benli Chu, Qiang Su. Improving the stability of alkaline earth sulfide-based phosphors // Applied Surface Science. 2003. Vol. 225. P. 198-203.

[14] Dorenbos P. The Eu3+ charge transfer energy and the relation with the band gap of compounds // Journal of luminescence. 2005. Vol. 111. P. 89- 104.

[15] Dongdong Jia, Jing Zhu, Boqun Wu. Influence of Co-doping with Cl2 on the Luminescence of CaS:Eu2+ // Journal of The Electrochemical Sosiety. 2000. Vol. 147. P. 3948-3952.

[16] Wartenberg H.Z. // Inorg., chem. 1943. Bd. 252. P. 136.

[17] Tiede, Richter F. dish., Chem. Ges. 1922. Bd. 55. P. 69.

[18] Jia D., Meltzer R.S., Yen W.M. Ce3+ energy levels relative to the bandstructure in CaS: evidence from photoionization and electron trapping // Journal of Luminescence. 2002. Vol. 99. P. 1-6.

[19] Kazuhiro Nagata, Kazuhiro S Goto. Ionic conductivity of solid calcium sulfide at 650 to 1000 °C // Metallurgical transaction. 1974. Vol. 5. P. 899-902.

[20] Vijay Singh, Manoj Tiwari, T. K. Gundu Rao, S. J. Dhoble. Luminescent studies of impurity doped SrS phosphors // Materials Research Bulletin. 2005. Vol. 28. P. 31-34.

А. Баешов, А. Е. Конурбаев, У. А. Абдувалиева,
Н. Б. Сарсенбаев, А. Б. Маханбетов, Д. А. Абижанова

Институт топлива, катализа и электрохимии им. Д. В. Сокольского, Алматы, Казахстан

ПОЛУЧЕНИЕ СУЛЬФИДА КАЛЬЦИЯ С ИСПОЛЬЗОВАНИЕМ ЭЛЕКТРОПРОВОДНОГО КОМПОЗИЦИОННОГО СЕРА-ГРАФИТОВОГО ЭЛЕКТРОДА ЭЛЕКТРОХИМИЧЕСКИМ МЕТОДОМ

Аннотация. Приведены результаты исследования электрохимического процесса получения сульфида кальция. Для данной цели использован специально изготовленный авторами электропроводный композиционный сера-графитовый электрод. В данном электроде сера и графит были взяты в соотношении 50:50.

Электрохимический синтез сульфида кальция проводился методом электролиза в электролизере с разделенными электродными пространствами. Для разделения электродных пространств электролизера применялась катионитовая мембрана – МК-40. На выход по току образования сульфид-ионов исследовано влияние таких параметров, как - плотность тока, концентрация гидроксида натрия и продолжительность электролиза. Установлено, что увеличение указанных параметров приводит к возрастанию значения выхода по току образования сульфид-ионов. Показано, что сера находящаяся в составе сера-графитового электрода, активно вступает в реакцию с кальций-ионами с образованием сульфида кальция. Максимальное значение выхода по току образования сульфида кальция, полученного электрохимическим методом, равняется 90%. Результаты рентгенофазового анализа и инфракрасной спектроскопии свидетельствуют об образовании сульфида кальция. Предлагаемый нами электрохимический способ получения сульфида кальция прост и экономически выгоден.

Ключевые слова: электрохимия, сера, графит, композиционный электрод, сульфид кальция, соотношение, выход по току, мембрана, токоподвод, синтез.

А. Баешов, А. Е. Конурбаев, У. А. Абдувалиева,
Н. Б. Сарсенбаев, А. Б. Маханбетов, Д. А. Абижанова

Д. В. Сокольский атындағы жанармай, катализ және электрохимия институты, Алматы, Қазақстан

ЭЛЕКТРӨТКІЗГІШТІ КОМПОЗИЦИЯЛЫ КҮКІРТ-ГРАФИТТІ ЭЛЕКТРОДТЫ ҚОЛДАНА ОТЫРЫП ЭЛЕКТРОХИМИЯЛЫҚ ӘДІСПЕН КАЛЬЦИЙ СУЛЬФИДІН АЛУ

Аннотация. Мақалада кальций сульфидін электрохимиялық жолмен алу процессін зерттеу нәтижелері келтірілген. Ол үшін авторлар арнайы дайындаған электрөткізгішті композициялы күкірт-графитті электроды қолданылды. Бұл электродта күкірт пен графит 50-50 ара салмақта алынды. Кальций сульфидінің электрохимиялық жолмен синтезі электродтық аймақтары бөлінген электролизерде электролиз арқылы жүргізілді. Электролизердің электродтық аймақтары катионитті мембрана МК-40 арқылы бөлінген. Сульфид-иондарының түзілуінің ток бойынша шығымына ток тығыздығы, натрий гидроксиді концентрациясы және электролиз ұзақтығы сияқты параметрлердің әсері зерттелді. Аталған параметрлердің мәндерінің жоғарылауы сульфид-иондарының түзілуінің ток бойынша шығымының жоғарылауына алып келетіндігі анықталды. Күкірт-графит электродының құрамындағы күкірт кальций-иондарымен белсенді реакцияға түсіп кальций сульфиді түзілетіндігі көрсетілді. Электрохимиялық жолмен алынған кальций сульфиді түзілуінің максимальді ток шығымы 90%-ға тең. Рентгенофазалық анализ және инфрақызыл спектроскопия нәтижелері кальций сульфиді түзілетіндігін көрсетті. Біз ұсынып отырған кальций сульфидін алудың электрохимиялық әдісі экономикалық жағынан тиімді әрі қарапайым болып табылады.

Түйін сөздер: электрохимия, күкірт, графит, композициялы электрод, кальций сульфиді, ара салмақ, ток шығымы, мембрана, тоқжолы, синтез.