- S.M. Lupinos (1), research worker, c.t.s.
- S.D. Ventsev (2), senior research worker, c.t.s.
- $V.M.\ Protsenko\ ^{(3)},$ associate professor, c.t.s.
- V.N. Kosenko (3), associate professor, c.t.s.
- N.P. Krivoruchko (4), main specialist

ABOUT POSSIBILITY OF ASSURING FOR PRODUCTION OF MAGNESIUM BY RAW MATERIAL OF DOMESTIC DEPOSITS

((1) SI «State and project Institute of titan», Zaporozhe, Ukraine ((2) Institute of E.O. Paton electric welding of NAS of Ukraine, Kyiv, Ukraine ((3) Zaporozhe state engineering academy, Ukraine ((4) SP «Zaporozhe titanium-magnesium combine» Ukraine

Introduction. Proceeding in the production of magnesium at LTD. «Magnesium» (c. Kalush) in Kalush, which in the last century structurally entered in the complement of PA «Chlorvinyl», in 2005 it was produced on the basis of deliveries and processing of brines of the Poltava bischofites. In 2008 a plant was shut-down for lack of stable deliveries of raw material. Its products (about six thousand tons in year at project power twenty two thousands tons) went, mainly, on an export and plant to a great extent provided the necessities of Western Europe. At the same time, proceeding in the production of commodity magnesium on LTD. «Magnesium» and on SP «ZTMC» possibly on the base of processing of Ukrainian magnesites.

Questions of geological structure of deposits and ore effects of magnesite are in Ukraine, their geo-economical estimation, possible directions of involving of ores in an industrial production and perspectives of the complex use of deposits are considered previously in works [1-6]. There is drawn conclusion, that as the Ukrainian deposits of magnesite were studied mainly in 50-60th of XX century, today, in connection with development of modern technologies, requirements substantially changed to the obtained raw material and expediency of realization of overvalue for all raw mineral-material base came to a head.

Deposits of talc-magnesites Ukraine. Two large deposits of talc-magnesites Pravdinsk and Veselyansk, and also row of perspective effects, are known in Ukraine. Veselyansk deposit of talc-magnesites openly in 1952-1955 and localized on the left slope of the river Konka, near s. Veselyanka of the Zaporozhe district of the Zaporozhe area in 25 km from Zaporozhe.

The most widespread variety of talc-magnesite is a greenish-grey rock, dense, fat by touch, roughlyslating. It is marked a good block - characteristic property of rocks, suitable for the fretwork of fire-brick. Content of minerals makes on a deposit, %, consist: magnesite – 46-92; talc – 42-77; magnetite – 1,5-10; quartz – 1,0-2,0; pyrite – to 1,0. Chemical composition of talc-magnesite is relatively permanent (mass. stake, %) : MgO - 18.5-36.6; $SiO_2 - 30.8$; $TiO_2 - 0.04$; $Al_2O_3 - 0.2-0.9$; $Fe_2O_3 - 0.1-4.5$; FeO - 4.5-6.6; MnO - 0.08-0.20; CaO - 1.28; $(Na_2O + K_2O) - 0.08-0.16$; $P_2O_5 - 0.02$; $SO_3 - 0.4-0.5$; NiO - 0.36; CoO - 0.028; $H_2O - 0.06-0.78$; $CO_2 - 25.0$; I.a.i. - 24.80. In rocks also there are elements-impurites: Cr, Zr, Cu, Pb, Ag, P, Zn. Serpentinites have next chemical composition, %: MgO - 37.25; $SiO_2 - 34.02$; $Al_2O_3 - 1.40$; $Fe_2O_3 - 3.43$; FeO - 4.60; CaO - 0.30; I.a.i. - 18,4.

From ores of Veselyansk deposits after concentration magnesite concentrate of such chemical composition, %, was got: MgO - 37.5-38.5; $SiO_2 - 2.1-2.3$; $Fe_2O_3 - 1.4-2.1$; FeO - 5.8-6.1; CaO - 2.5-3.0; $CO_2 - 46.5-48.0$. On content iron the got concentrate answers a breunerite.

Pravdinsk deposit of talc-magnesites and carbonatenizing serpentinites is located near s. Grushevka of Krinichansk district of the Dnepropetrovsk area in 25 km south of c. Dnepropetrovsk. A deposit is located in south-west part of the same name ultrabasis massif which enters in Westsursk stripe of ultraalkalites. On a deposit two types of ores are distinguished: talc-magnesite rocks and carboratenizing serpentinites.

Talc-magnesite rocks (talc-magnesites) consist of talc (35-50 %) and magnesite (40-60 %) and negligible quantity of serpentine (antigorite), dolomite, magnetite and chlorite. The content of carbonate in them arrives 15-93 %. The mass stake of basic chemical components makes, %: MgO - 32-36; $SiO_2 - 25-30$; $Al_2O_3 - below 2$; CaO - below 2.

Carbonatenizing serpentinites consist of serpentine (of lysarditea, antigorite, sicklefitea (60-80 %), carbonate (*Ca-Mg-Fe*) (20-40 %), including. magnesite (10-30 %), talc, magnetite and chromite.

In 2010 within the limits of south-east part of Verkhovtsevsk greenstone structure there is investigational geological survey works Sukhokhutorskarea of talc-magnesites ores, timed to the of the same name massif of varvarovsk intrusive complex of archaean age.

Two types of ores prevail are on an area: serpentinites and talc-magnesites. Between them there are gradual transitions and there are relicts of serpentinites in the layer of talc-magnesites. Serpentinites are massive (sometimes striated) dense rocks, mainly even greenish-grey, rifle-green, bluish-darkly-green colouring. Mineralogical composition, %: serpentinite – 50-95; relict olivine – 0-45; magnesite – 2-15; carbonate – 10-15; talc+chlorite – to 5-10; accessory – chromspinelides, ore – pentlandite and chalcopyrite.

Chemical composition of talc-magnesites ores of Sukhokhutorsk area is characterized by constancy of chemical composition both on extending and on the depth of ore beds (table 1).

Content of components, %	SiO ₂	Al_2O_3	СаО	MgO	MgO/SiO ₂
min	5.0	0.10	0.25	32.0	1.04
max	34.0	5.20	9.60	45.5	9.04
middle	30.34	0.48	1.93	37.59	1.26

Table 1 – Chemical composition of talc-magnesites ores of Sukhokhutorsk area

The complex estimation of Capitanovsk ore field where is in Tarnovatsk massif magnesium ores are educed presently conducted. They are presented by the ore bodies of oblong lentiform form long a 100-1000 m and more and by power from a 20-60 m a to 600 m. Chemical composition of serpenyinites following, %: MgO - 40.20; $SiO_2 - 32.60$; $TiO_2 - 0.06$; $Al_2O_3 - 0.66$; $Fe_2O_3 - 6.90$; FeO - 2.61; MnO - 0.08; CaO - 0.29; $P_2O_5 - 0.02$; $K_2O - 0.06$; $Na_2O - 0.06$; $SO_3 - 0.13$; $Cr_2O_3 - 0.43$; NiO - 0.39; CoO - 0.01; $H_2O - 0.22$; l.a.i. -15.09. Mineral composition of magnesium ores is presented by a chrysotile (pre-

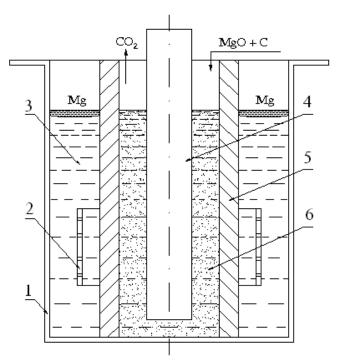
vailing mineral), lysardite, sicklefite, bastite, spinel and carbonates. Also in this deposit the supplies of chromite and silicate-nickeliferous ores are concentrated.

It is assumed that these objects will fill up the raw mineral-material base of magnesium of Ukraine. Thus, objects of Capitanovsk the ore field are complex, and except for magnesite expediently also to distinguish the chromite concantrates and concentrates of silicate nickel. Also from magnesium ores it is additionally possible to get a nickel-cobalt concentrate, oxide of iron, clean silica, gold, metals of platinum group [6].

Technologies of receipt of magnesium from magnesite. As the most perspective method in 80th of XX century on technics-economy estimations the method of electrowinning of magnesium from oxide raw material was examined, allowing not only to organize an unchloric production, but maximally to shorten the technological chart of production, providing the same the minimum prime price of the got magnesium. Development of technology was carried out by the specialists of Institute of titan and MISandA [8-10].

The feature of technology was a division of anolyte and katholyte by a porous diaphragm, which provided the transport of ions of electrolyte, but was impenetrable for particles oxide-coal charge. The chart of electrolyzer with a porous diaphragm is brought on a fig. 1.

Technology was tested on experimental electrolyzers with force of current 250-1000 A, the output of magnesium on a current in separate periods arrived 80-90 % at absence of chlorine in off-gas. However satisfactorily to decide the question of diaphragm capacity, providing its necessary firmness in chloride fusions and transport properties, unfortunately, was not succeeded.



1 is crucible; 2 is a steel cathode; 3 is a katholyte; 4 is a graphite anode; 5 is a porous heat-resistant diaphragm; 6 is an anolyte

Figure 1 – Chart of electrolyzer with a porous diaphragm for the receipt of magnesium from oxide raw material:

The technological chart of extraction of magnesium from serpentinite or wastes productions of asbestos, based on the salt acid lixiviating of ore and subsequent processing of chlormagnesium solutions and siliconcontaining remain is known [11]. Other technology is based on lixiviating of oxide magnesium raw material by an ammonium chloride [12].

However industrial realization of these technologies requires substantial capital costs and floorspaces on creation and exploitation of hydrometallurgical redistribution.

More short technological and less a capitalinvensiven way is worked out in SP «Institute of titan», where in 2010-2013 the complex of works is executed [13-18], finishing development bases of high-efficiency technology of production of chlormagnesium fusions from magnesites for the electrowinning of magnesium.

During research of mechanism and kinetics of process of chlorinating in presence a hard repairer [13,15] expediency of replacement of hard repairer, used in a process, on gaseous (an oxide of carbon) is shown. At research of mechanism of co-operation of magnesite with mixture of chlorine and oxide of carbon diffusive nature of process is set, conformities to law of masstransfer in the system are studied, by theory and an experimental way the conditions of equal delivary of gas reagents are certain to surface of the chlorinated magnesite [13]. It allowed to attain in laboratory and large laboratory researches of max speed of process of chlorinating at the practically complete mastering of chlorine.

The worked out technology is realized on the pilot appapatus in the chlorinator of mine type with the internal diameter of mine a 0.3 m [16]. The mass stake of components in the fusion of dichloride of magnesium got on appapatus for period of tests made, %: $MgCl_2 - 97.0-98.8$; $CaCl_2 - 0.7-1.2$; MgO - 0.3-0.6; $SiO_2 - 0.008-0.04$; $Fe_{gen} - 0.001-0.006$; Al - 0.001-0.004; $SO_4 < 0.02$. On content basic impurites the got product fully conditions electrolytic redistribution for all types of electrolyzers, exploited in countries the CIS.

By comparison with the before exploited technology of chlorinating of magnesite, new technology, foreseeing preliminary gasification of repairer, allows:

- substantially to shorten and simplify the apparatus-technological chart of preparation of raw material to the process of chlorinating (seven redistributions are removed), to lower capital-intensiveness of technology;
- to promote speed of chlorinating of magnesite and specific productivity of hypochlorinator in three times (to 6.5-7.0 t $MgCl_2/m^2$ ·twenty-four hours);
- to lower maintenance of impurites and improve quality of the got chloride fusion, that allows to improve the indexes of subsequent process of electrolytic renewal of chloride and improve quality producible electrolytic magnesium;
- to attain practically the complete use of chlorine in a process, that stipulates reduction of his specific expense and decline of expenses on scrubber;
- to reduce the specific expense of raw material on 10 %, to decrease a specific energy consumption on 15-20 %, to promote economic efficiency of technology.

At industrial registration of the worked out technology it will give the substantial decline of capital costs and prime price of the got fusion of chloride of magnesium and producible from him magnesium. The got results allow really to examine magnesite as effective raw material for processing with the use of chloric technologies in magnesium industry.

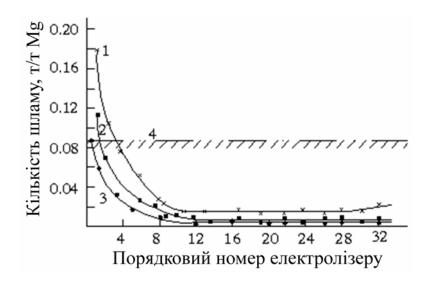
In the brought research-and-developments over magnetite's Kirgitajsk and Satka of deposits (Russian Federation) is used with insignificant maintenance of impurities (to 2.0-3.0 %). Processing of Ukrainian magnetite's, which content of concomitant minerals is higher in, probably, will demand the preliminary technological assay of their ores and, possibly, development of cleaning methods from concomitant impurities.

Nevertheless, presence of the developed infrastructure in the district of localization of deposits, possible moderate running expenses at his development, allow to examine deposits, as perspective enough. Especially taking into account that Veselyanskoe deposit

located in 25-30 km from the Zaporozhe enterprises – titan-magnium combine (SE «ZTMC»), PAS Plant of semiconductors and PAS «Zaporozherefractory».

It creates the certain prospect of the complex use of his ores [5], especially, if with the use of methods of the selective and complex chlorinating siliconcontaining minerals will succeed to be unsealed with the receipt of chlorides of silicon and subsequent production of technical or polycrystalline silicon. Potential possibility of extraction of silicon as chlorides is marked earlier [19] at research of chlorinating of titan-silicon concentrates. Other prospect for the complex processing is possibility of extraction in the process of chlorinating and division of Ni, Co, Cr, Zr, Cu and other concomitant elements.

Taking into account higher content of impurities in domestic magnesites, electrolytic processing of the got fusion of chloride of magnesium, probably, it is expedient to organize in the production line of electrolyzes [20-21]. Experience of operation and maintenance phase of production line showed that in the head vehicle of line the gravity cleaning of fusion of electrolyte can be carried out from the hard dredges of particles of non chlorinated magnesite, including MgO and SiO_2 (figure 2).



Figture 2 is quantity of pulp, deleted from the electrolyzers of production line: 1 is a total quantity of deleted pulp; 2 is pulp, pumped out with pulp-electrolite mixture; 3 is pulp of hand selection; 4 is a quantity of pulp at individual maintenance of electrolyzer

And in the refinery electrolyzers of production line the effective electrocleaning of fusion will be carried out from the impurities of more electropositive metals, acting's in the process of chlorinating in fusion, including. from the chlorides of iron.

Conclusions. The overvalue of raw mineral-material base of magnesite of Ukraine was not conducted the last years. However, taking into account that presently economic and industrial requirements changed to this raw material, it is expedient to conduct the additional technological assay of perspective objects and execute their overvalue. It will allow to extend a raw mineral-material base for heat-resistant and magnesium industry. A question about efficiency of the use of magnesites Veselyanskoro and other Ukrainian deposits in metallurgical industry for the production of magnesium and other concomitant elements can be decided on the

basis of preliminary research and technological assay of ores and concentrates of these deposits.

REFERENCES

- 1. Бондарчук, В. Г. Геологія родовищ корисних копалин України [Текст] / В. Г. Бондарчук. Київ : Наукова думка. 1966. 302 с. Бібліогр. : с. 291-298.
- 2. Бордюгов, В. П. Магнезит и талько-магнезит (геолого-экономический обзор) [Текст] / В. П. Бордюгов. Киев : Геоиформ, 1997. 25 с.
- 3. Комов, И. Л. Геологические и геолого-экономические черты метаморфогенного сырья Украинского щита [Текст] / И. Л. Комов, Е. А. Кулиш // Збірник наукових праць Інституту геохімії навколишнього середовища. Київ : 2002. Вип. 5-6. С. 184-198.
- 4. Перспективы освоения минерально-сырьевой базы магнезита Украины [Текст] / Л. С. Галецкий, Е. А. Ремезова, С. М. Лупинос и др. // Геологічний журнал. 2012. № 1. С. 48 -56.
- 5. О возможности комплексного использования месторождений талько-магнезитов Украины (на примере Веселянского месторождения) [Текст] / Л. С. Галецкий, Е. А. Ремезова, С. М. Лупинос и др. // Нові матеріали і технології в металургії та машинобудуванні. 2012. № 2. С. 100-105.
- 6. Бочевар, Р. О. Геолого-економічна оцінка комплексних руд Капітанівського рудного поля (Голованівська шовна зона) [Текст] : автореф. Дис. ... канд. геол. наук : 04.00.19 «Економічна геологія» / Р. О. Бочевар. Київ, 2012. 20 с.
- 7. Стрелец, Х. Л. Металлургия магния [Текст] / Х. Л. Стрелец, А. Ю. Тайц., Б. С. Гуляницкий. М. : Металлургия, 1960. 480 с. Библиогр. : с. 477-479.
- 8. Венцев, С. Д. Разработка теории и технологии электролитического способа получения магния с применением оксидно-углеродной шихты [Текст] : автореф. дис. ... канд. техн. наук / С. Д. Венцев. М., 1986. 25 с.
- 9. Абрамов, В. Я. Методика определения констант массообмена в электролизере с пористой диафрагмой [Текст] / В. Я. Абрамов, В. М. Проценко, Ю. Н. Чаусов // Цветные металлы. 1988. № 9. С. 73-74.
- 10. Абрамов, В. Я. Массообмен в магниевом электролизере с диафрагмой [Текст] / В. Я. Абрамов, В. М. Проценко // Цветные металлы. 1988. № 11. С. 65-67.
- 11. Фрейдлина, Р. Г. Комплексная переработка промышленных отходов с получением сырья для производства магния и кремнеземной продукции [Текст] / Р. Г. Фрейдлина, В. И. Грибов // Цветная металлургия. 2010. № 6. С. 29-37.
- 12. Исследования по подготовке оксидного магниевого сырья к электролитическому получению магния [Текст] / В. И. Щеголев, А. Н. Татакин, А. Б. Безукладников и др. // Цветные металлы. 2000. № 1. С. 52-55.
- 13. Прутцков, Д. В. Закономерности механизма взаимодействия магнезита со смесью хлора и оксида углерода и массоперенос в рассматриваемой системе [Текст] / Д. В. Прутцков, С. М. Лупинос, Ю. М. Рябухин // Теория и практика металлургии. 2010. № 3-4 (76-77). С. 110-116.
- 14. Лупинос, С. М. Разработка технологии получения хлормагниевых расплавов из природного карбоната магния [Текст] / С. М. Лупинос, Д. В. Прутцков, А. Н. Петрунько // Металлургическая и горнорудная промышленность. 2010. № 4 (262). С. 98-102.
- 15. Лупинос, С. М. Исследование процессов хлорирования оксидного магниевого сырья с использованием твердого восстановителя [Текст] / С. М. Лупинос // Металлургическая и горнорудная промышленность. 2011. № 2 (267). С. 75-79.
- 16. Прутцков, Д. В. Исследование процесса хлорирования магнезита смесью хлора и оксида углерода на пилотной установке [Текст] / Д. В. Прутцков, С. М. Лупинос, Н. П. Криворучко // Металургія : наукові праці Запорізької державної інженерної академії. Запоріжжя : РВВ ЗДІА, 2010. Вип. 21. С. 33-43.
- 17. Лупинос, С. М. Влияние состава расплава на кинетику процесса хлорирования карбоната магния смесью хлора и оксида углерода [Текст] / С. М. Лупинос, Д. В. Прутцков, Ю. А. Динник // Теория и практика металлургии. 2011. № 3-4 (82-83). С. 78 82.

- 18. Лупинос, С. М. Исследование поведения примесей в процессе хлорирования магнезита [Текст] / С. М. Лупинос // Металургія : наукові праці Запорізької державної інжернерної академії. Запоріжжя : PBB ЗДІА, 2013. Вип. 1 (29). С. 29-36.
- 19. Дрожжев, В. И. Переработка титано-кремниевых концентратов методом хлорирования [Текст] / В. И. Дрожжев, В. А. Ильичев // Металлургия и химия титана : научные труды Института титана. М. : Металургія, 1968. Т. 2. С. 105-110.
- 20. Зуев, Н. М. Исследование и разработка поточной технологии электролитического производства магния [Текст] : дис. ... докт. техн. наук / Н. М. Зуев. Л., 1975. 327 с.
- 21. Бачурский, Д. В. Особенности электролитического производства магния в поточной линии [Текст] / Д. В. Бачурский // Металургія : наукові праці Запорізької державної інженерної академії. Запоріжжя : РВВ ЗДІА, 2008. Вип. 18. С. 69-72.
- 22. Производство магния на заводе фирмы Dead Sea Magnesium [Текст] / 3. Рубинович, Г. Кацнельсон, Р. Эцион, Е. Агион // Цветные металлы. 2002. № 10. С. 61-64.