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**Complex
Use of
Mineral
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The effect of blend copolymers on physico-mechanical properties of mortar

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Abstract. The present study investigates the effect of blend copolymers on the physico-mechanical properties of mortar mixes. Blend copolymers were synthesized based on poly vinyl alcohol (PVA) and urea (U) in aqueous solution with different blend ratios 65/35, 50/50 and 35/65 respectively, using glacial acetic acid as crosslinking. Physico-mechanical properties of mortar examined included water/cement ratio, setting time, workability, water absorption and compressive strength. The addition of blend copolymers to the mortar affected the physico-mechanical properties of mortar mixes. As the content of PVA increases in the blend copolymers, the water of consistency decrease, whereas the setting times (initial & final) were shortened. The compressive strength of the hardened cement pastes was increased at all ages of hydration while water absorption decreased.

Keywords: Mortar, PVA, urea, cement, compressive strength, workability.

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Introduction

A number of researchers have studied the addition of chemical admixture to building materials based on polymeric compounds to improve the physical and mechanical properties of cement pastes, mortar and concrete [1-10, 30-31]. The main mechanism of improving properties of cement with addition of polymers is a thin film formed on the surface of grains of cement, aggregate, as well as pores which gave more adhesion [2-6].

Polyvinyl alcohol (PVA) is a water-soluble polymer and used in the industry as a modifier, as aggregate surface pre-treatment agent and as reinforcement in cement-based materials because of its chemical resistance and physical properties [3, 6]. Generally, PVA is added in the form of aqueous solution in small amounts (up to 2% based on the weight of cement during mixing) to improve the properties of cement mortar and concrete product [3, 8]. Negim *et al.* [11, 12] investigated the physical and mechanical properties of mortar containing PVA and

dodecyl benzene sodium sulfonate as an air entraining agent. Additionally, PVA and dodecyl benzene sodium sulfonate were used to prepare copolymers latex: styrene/butyl methacrylate, styrene/methyl methacrylate, styrene/glycidyl methacrylate and styrene/ butyl acrylate. The results showed that PVA improved workability of mortar mixed as well as copolymer latex. Copolymer latexes based on 2-hydroxy ethyl acrylate and 2-hydroxy ethyl methacrylate. Different molar ratio of 2-hydroxy ethyl acrylate and 2-hydroxy ethyl methacrylate was designed to investigate the effect of latexes on the physico-mechanical properties of mortar. The copolymer latexes reduce water of consistency of mortar and increased workability [13]. The effect of concentration of styrene/butyl acrylate latexes on properties of mortars was investigated [14]. If the concentration of polymer is more than 5%, there is no significant influence on the properties of mortar mixes.

Negim et al. [15] prepared blend polymers based on polyvinyl alcohol (PVA) and urea (U) in different ratios, using glacial acid as catalysis. The addition of blend polymers to cement pastes improved the properties of cement pastes [16]. The work was extended to include the application of blend polymers to study physical and mechanical properties of mortar.

Experimental part

Materials: Polyvinyl alcohol (PVA) of molecular weight 14×10^3 g/mol purchased from Merck (Germany). Urea (U) and glacial acetic as catalysis purchased from Aldrich. The raw materials used in the present study are Portland cement clinker (PCC) and raw gypsum (G). Each of those raw materials was separately ground in a steel ball mill until the surface area of respectively was 3650 and 2800 cm^2/g . The mineralogical composition of the PCC sample is C_3S , 58.79 %; $\beta\text{-C}_2\text{S}$, 17.68 %; C_3A , 8.08 %; C_4AF , 9.72 %. The Portland Cement (PC) was prepared by mixing 96 % PCC and 4 % G (by weight) in a porcelain ball mill for one hour using 3 balls to ensure complete homogeneity of the cement. The Blaine surface area of the cement sample was 3350 cm^2/g [17].

The fine aggregate was sand with particle size ranging from 0.21mm to 0.53 mm and is free from organic or clay-like materials.

Synthesis and characterization of copolymers: Copolymer blend based on polyvinyl alcohol (PVA) with urea (U), were synthesized with composition ratios 65: 35 (M1), 50: 50 (M2) and 35: 65 (M3) glacial acetic acid as catalysis. The preparation of copolymers and the methods of analysis (^1H NMR, rheological and morphological

techniques) have been previously described in a previous investigation [15].

Mixing and testing: Mortar specimens of size 70 mm cube were prepared in three groups. The control mix (M0) consists of Portland cement (PC), sand and water. The proportion of cement to sand was 1:3 (by weight) (M0). In mixes M1-M3, prepared copolymers blends were added. The addition rate was 2% by weight of cement. The cement to sand ratio was kept constant. However, the water to cement ratio was changed so that the same consistency was achieved.

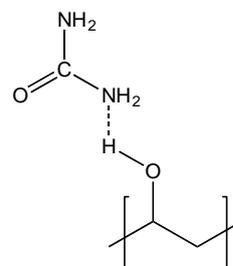
The cement and sand were intermixed until homogeneity was achieved. Then the surfactants or prepared latexes were added to the mixing water. This was then added gradually to cement/sand mixture in order to determine the water of consistency and setting time using Vicat apparatus [18, 19].

The resulting mortar was directly placed into 70 mm cube stainless steel moulds. The moulds were manually agitated for 2 minutes and then on a vibrator for another 2 minutes. The moulds were kept in a humidity chamber at 100 % R. H and a constant room temperature overnight, then demoulded and cured under water till the time of testing. Testing included compressive strength, water absorption and combined water and was conducted at 1 day, 3, 7 and 28 days.

The determination of water absorption as per the specifications of BS 1881: Part 122 [20], compressive strength, water absorption and combined water were described in a previous investigation by the authors [21].

Results and Discussion

Structure of Copolymers: The structure of the copolymers blend P(PVA-b-U) is shown in Scheme 1 and further details about the synthesis and characterization have been previously reported by the authors [15].



Scheme 1 Structure of P(PVA-b-U).

Water/ cement ratio (W/C): The results of water consistency of mortar mixes are graphically illustrated in Figure 1. The water-to-cement ratio is

one of the most important items in all tests because special failures associated with the cement structures are essentially due to either too much or too low water that is added during mixing [22]. The W/C ratio for mortar mix without polymer was 0.525. The premixed grafting polymer with mortar mixes decreases W/C ratio from 0.525 to 0.49 (M1). However, increasing the PVA content in the blend copolymer decreases the W/C ratio of the mortar mixes.

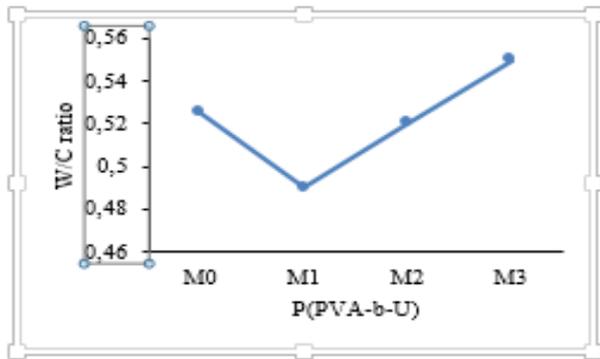


Figure 1 The effect of blend copolymer on W/C ratio of mortar.

Setting time: The setting time (initial and final) of mortar premixed with blend copolymers are given in Figure 2. The setting time of mortar extends with the addition of blend copolymers to mortar. From Figure 2, it is clear that, as the content of PVA in the blend copolymers increases, setting times decreased. This is fundamentally because of the water losing by evaporation from the external surfaces of the samples mixed with the blend copolymer is generally not as much as that of the control mortar mix [23].

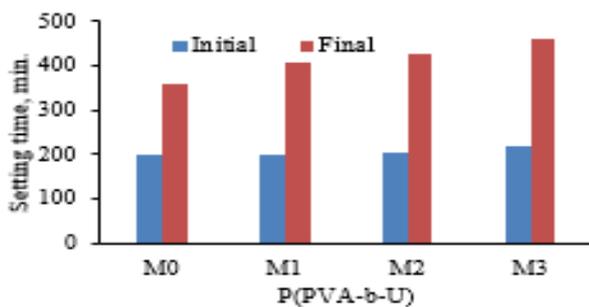


Figure 2 The effect of blend copolymer on setting time of mortar.

Workability: The results of the mortar workability tests are shown graphically in Figure 3. The outcomes demonstrate that the workability of mortar without polymer (M0) is 128 mm; but there was an expansion in workability estimation with the addition of blend copolymer. This expansion in workability was attributed to the blend copolymer

being a surface-active agent. Figure 3 shows sharp increase in flow of mortar with increasing the content of PVA in the blend copolymer. Mortar mixed with 65% PVA gave the highest flow with 190.4 mm while mortar mixed with 35% PVA gave the lowest flow with 158.7 mm. Increasing of the mortar workability is principally determined as far as enhanced consistency because of both the 'ball bearing' activity and the dispersing impact of polymer [24].

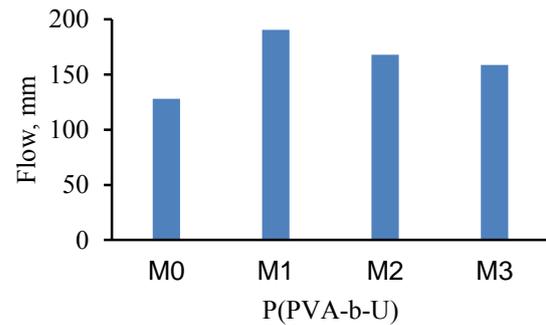


Figure 3 The effect of blend copolymer on workability of mortar.

Water absorption: For the most part, the contact of cement in mortar with water, cement retains water in view of its permeable microstructure. The lower the water absorption, the lower the porous pore volume [25].

The effect of blend copolymer with different content of PVA on water absorption of mortar is demonstrated graphically in Figure 4. It is clear that the water absorption of the mortar mixed with blend copolymer decreased with the increasing of PVA content in the blend copolymer. This is ascribed to the hydration procedure occurring. Different investigations additionally demonstrated that the polymer fills the voids in the cement grid [26, 27]. Polymer-modified mortars are therefore expected to be more resistant towards penetrating aggressive environments than control mix.

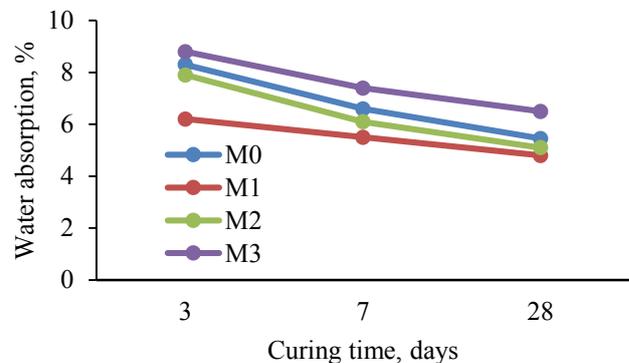


Figure 4 The effect of blend copolymer on water absorption of mortar.

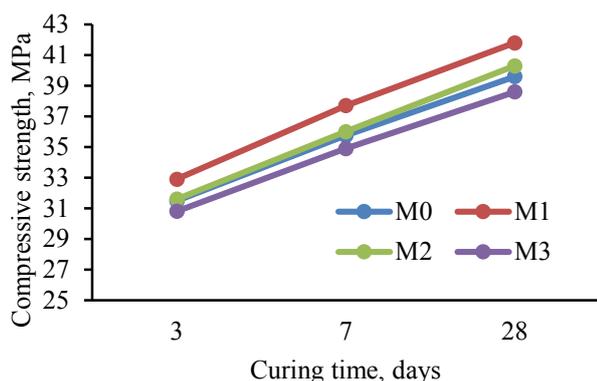


Figure 5 The effect of blend copolymer on compressive strength of mortar.

Compressive strength: Compressive strength of mortar increased with addition blend copolymer to mortar mixes as shown in Figure 5. As appeared from Figure 5, the compressive strength of mortar premixed with blend copolymer (M1, 65% PVA) is higher than that of mortar mixed with blend copolymer (M2, 50% PVA) and (M3, 35% PVA) at all curing periods. This is chiefly because of the adhesive activity due to polymerization or crystallization of the polymeric materials the excess of polymers deposits and polymerizes inside the pore arrangement of the solidified mortar cubes. The development of crystalline structure goes about as nuclei for different components. This may keep on enlarging precious crystals and solid arms-bearing high strength [28]. The consequences of compressive strength of mortar blended with united. This tends to enhance and upgrade the mechanical properties of the mortar cubes. Moreover, the higher level of polymerization and the higher powers between the particles of cement and those of the polymeric

materials are the fundamental elements in charge of the generally higher compressive strength [29].

Conclusions

Based on the results of the conducted studies, it is possible to conclude the following:

➤ The addition of blend copolymers (M1; 65% PVA & M2; 50% PVA) to the mortar mixes improves most of the specific characteristics of the mortar;

➤ The addition of blend copolymer to mortar decreases water/ cement-ratio decreases, i.e. the blend copolymer acts as a water reducing agent when mixed with the mortar;

➤ Setting time of mortars increased with increasing the content of PVA in the blend copolymers.

➤ The flow table results showed that the blend copolymer enhances workability of mortars specially with 65% PVA.

➤ Water absorption of the mortar premixed with the blend copolymers (65% & 50% PVA) decreased while with blend copolymer 35% PVA increased.

➤ Compressive strength of mortar increased sharply compared with those of the reference mortar.

➤ As the ratio of PVA in the blend copolymer increased, the properties of the mortar also improved.

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Аралас сополимерлердің цементті ерітіндінің физика-механикалық қасиеттеріне әсері

Л. Бекбаева, Эльсайд Негим, Г. Елигбаева, Е. Ганжиан

Түйіндеме. Бұл зерттеуде аралас сополимерлердің құрылыс ерітіндісінің қоспаларының физико-механикалық қасиеттеріне әсері қарастырылды. Аралас сополимерлер 65/35, 50/50 және 35/65 қоспаларында әртүрлі қатынастағы поливинил спиртінің (ПВС) және мочевианың (М) судағы ерітіндісі негізінде, мұзды сірке қышқылын тіккіш қосылыс ретінде пайдалана отырып синтезделді. Зерттелетін ерітіндінің физико-механикалық қасиеттеріне жататын: су / цемент қатынасы, қатаю уақыты, қозғалғыштығы, суды ұстағыштығы және қысуға беріктік күші белгіленді. Аралас сополимерлерді құрылыс ерітіндісіне қосу, ерітіндінің қоспаларының физико-механикалық қасиеттеріне әсер етті. Аралас сополимерлердегі ПВС құрамының артуы салдарынан судың құрамдылығы азайып, қатаю уақыты (бастапқы және соңғы) қысқарды. Қатайған цемент пасталарының су сіңіргіштігі төмендеп, беріктігі сығылу күшінің барлық гидратациясының ұлғаюымен бірге өсті.

Түйін сөздер: құрылыс ерітіндісі, ПВС, мочевина, цемент, сығылу күші, қозғалғыштығы.

Влияние смесевых сополимеров на физико-механические свойства цементного раствора

Л. Бекбаева, Эльсайд Негим, Г. Елигбаева, Е. Ганжиан

Аннотация. В настоящем исследовании исследуется влияние смешанных сополимеров на физико-механические свойства строительных растворов смесей. Смешанные сополимеры были синтезированы на основе поливинилового спирта (ПВС) и мочевины (М) в водном растворе с различными соотношениями смесей 65/35, 50/50 и 35/65 соответственно, с использованием ледяной уксусной кислоты в качестве сшивки. Физико-механические свойства исследуемого раствора включали соотношение вода / цемент, время схватывания, подвижность, водо-поглощение и прочность на сжатие. Добавление смешанных сополимеров в строительный раствор влияло на физико-механические свойства растворов смесей. По мере увеличения содержания ПВС в смешанных сополимерах консистенции воды снижалась, тогда как время схватывания (начальное и конечное) сокращалось. Прочность при сжатии затвердевших цементных паст увеличивалась при всех возрастании гидратации, тогда как водо-поглощаемость уменьшалась.

Ключевые слова: строительный раствор, ПВС, мочевина, цемент, прочность на сжатие, подвижность.

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Синтез высокодисперсных форм оксида цинка легированных редкоземельными элементами (обзор)

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Аннотация. В работе обобщены литературные данные, рассмотрены способы получения высокодисперсных форм оксида цинка легированных редкоземельными элементами. Легирование ZnO редкоземельными и 4d переходными элементами является популярным методом манипулирования оптическими свойствами систем ZnO. Эти системы могут также обладать собственным ферромагнетизмом из-за их магнитного момента, передаваемого на 4f и 4d электроны. Изложены также исследования авторов в этой области, имеющих целью использование ZnO в композитах металл/оксид: изучены свойства порошков оксида цинка легированных РЗМ, полученных различными технологическими методами. Были изучены работы по получению описанных структур, подбор лучших технологических параметров роста тонких плёнок. В связи с развитием нанотехнологии, соединения РЗЭ приобрели еще большую популярность и используются для получения нанолюминофоров, тонких пленок, микропористых мембран, золь-гель стекол.

Ключевые слова: оксид цинка, редкоземельные элементы, люминофоры, метод CVD, гидротермальный метод, микропорошок.

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Введение

Сегодня чистые и возобновляемые источники энергии очень важны из-за дефицита ископаемого топлива и экологических проблем. Полупроводниковые материалы с различными структурами и морфологией используются в различных областях исследований и разработок чистой и возобновляемой энергии из-за их уникальных характеристик [1-3, 27-29]. Структура, морфология и свойства полупроводниковых материалов связаны не только с материалами-предшественниками и методами получения, но также с примесью и температурами отжига [4-6]. Среди полупроводниковых материалов ZnO с широкой

зонной щелью (3,37 эВ) является полупроводником II-VI и обладает большой энергией связи экситонов 60 мэВ [7-8]. ZnO обладает отличными физическими и химическими свойствами, которые делают его уникальным материалом для многих устройств путем легирования различными ионами редкоземельных элементов [9]. Наноразмерные материалы обладают широким спектром электрических, магнитных и оптических свойств, вызывая активность мирового научного сообщества в получении, исследовании фундаментальных свойств, поиске практического применения различных форм нанокристаллических материалов (нитей, лент, тетраподов, пружин и т.д.). Отсутствие центра

симметрии у вюрцитной сингонии, к которой принадлежит ZnO, приводит к появлению пьезоэлектрических и пироэлектрических свойств, позволяя моделировать активные элементы для нужд нанопьезоэлектроники. ZnO является перспективным материалом для создания УФ излучателей, спин-функциональных приборов, газовых сенсоров, прозрачной электроники, приборов на поверхностных акустических волнах, и др. [10]. В то же время ZnO имеет ряд преимуществ, таких как более высокое значение энергии связи экситонов и возможность реализации ряда наноструктур при невысоких затратах [11]. Эти преимущества позволяют создавать лазеры, работающие при высоких температурах [12]. Ряд наноструктур, таких как нанонити [13], нановолокна [14], наноиглы [15] являются превосходными полевыми эмиттерами. Таким образом, при условии разработки высокоэффективных люминофоров на основе микро- и наноструктурированного ZnO, этот материал имеет наибольшие перспективы для создания полностью интегрированного дисплея с полевой эмиссией. Легирование редкоземельными металлами (РЗМ) данного полупроводника, открывает перспективы создания светоизлучающих приборов (LED) на заданную длину волны как в видимой (при легировании Tm, Er, Eu), так и ближней инфракрасной (при легировании Yb, Sm, Er) областях спектра. Приборы на основе ZnO, легированные РЗИ (Er, Ho, Nd, Pr), могут работать при повышенных температурах, при повышенных воздействиях ионизирующих излучений [5], поскольку температурный спад внутрицентровых переходов обратно пропорционален величине ширины запрещенной зоны. Легирующие примеси при создании LED подбираются по длине волны внутрицентровых переходов РЗМ. При этом необходимым условием является также реализация интенсивного излучения на заданной длине волны или получение интенсивного излучения для LED белого цвета, т.е. для твердотельного освещения. Все эти требования могут быть удовлетворены лишь при высокой эффективности легирования полупроводниковой матрицы. Парк и др. [16] изготовили люминофоры ZnO:EuCl₃ в различных внешних средах и при разных температурах и исследовали оптимальные условия для взаимодействия Eu и ZnO с целью получения чистого красного излучения. Однако Фуджихара и др. [17] предположили, что люминофор, изготовленный Парком и др. представляет собой на самом деле смесь ZnO и EuOCl, и красное излучение исходит

от кристаллитов EuOCl. В свою очередь Фуджихара и др. изготовили тонкопленочный красный люминофор на основе нанокompозита ZnO:(La,Eu)OF, в котором наночастицы (La, Eu) OF были внедрены в матрицу ZnO, и показали, что ионы Eu³⁺ внедрены практически в решетку LaOF, а механизмом возбуждения является перенос заряда между ионами Eu³⁺ и O²⁻.

В работах Аль Рифаи [18] проведено исследование микроструктурных и оптических свойств легированных нанонитей ZnO. Монокристаллические легированные микро и нанонити ZnO были синтезированы методом CVD без использования дополнительных катализаторов. Наноструктуры были выращены на стенах алундовой лодочки (тигля). Структура и свойства легированных нитей ZnO полностью характеризуется с помощью XRD, EDX, СЭМ, ПЭМ, ФЛ методов. Синтез проводился в течение 10 мин, в результате которого получены вертикально ориентированные нанонити диаметром 50-400 нм и длиной до нескольких микрон. Нанонити вытянуты вдоль с-оси в направлении \pm [0001]. Концентрация легирующей примеси в нанонитях оказалась равна 0,8 атомных %. Кристаллическая структура и свойства легированных образцов были проанализированы в сравнении с нелегированным ZnO. Самоорганизующиеся тетраподы были выращены без использования каких-либо затравок по механизму роста VS («пар-кристалл»). Между тем, VLS механизм предполагает использование катализаторов (обычно Au, Pt и др.) и обычно обуславливает рост нанонитей или наностержней с аналогичными размерами и параллельной ориентацией. Таким образом, предполагается, что порошок оксида европия (III) играет две роли в процессе синтеза. Во-первых, он имеет решающее значение для подготовки роста за счет поглощения паров Zn. Во-вторых, он осаждается на поверхности тигля в виде нанокapель европия, которые не только обеспечивают шаблоны для дальнейшего роста, но и обуславливают вертикально ориентированный рост, что приводит к выравниванию нанонитей с успешно включенным в решетку оксида цинка европием. На начальной стадии роста, пар Zn с растворенными частицами европия образует жидкий расплав. После пересыщения, пар с наночастицами европия реагирует с кислородом, осаждаясь тонким слоем капель на тигле, одновременно являющимся подложкой. Первый этап роста происходит по механизму «пар-жидкость-кристалл». Обильное прибытие паров ZnO делает наиболее вероятным рост по

механизму «пар-кристалл», как следствие, наночастицы катализатора инкапсулируются в кристаллическую решетку оксида цинка. Таким образом, на втором этапе синтеза, когда VLS рост еще не прекратился, но механизм VS уже начинает преобладать. На последней стадии процесса роста, частицы катализатора изолированы от паров реагента и не играют никакой роли. Как результат, механизм «пар-кристалл» (VS) способствует дальнейшему росту нитей ZnO.

Известно что ZnO легированные редкоземельными элементами оказывают существенное влияние на люминесценцию, химическую и поверхностную модификацию ZnO. В следующей работе [19] один из лантаноидных элементов Y использовался в качестве легирующей добавки для улучшения газочувствительности ZnO. Авторами были использованы многие методы синтеза для получения наночастиц оксида цинка, включая химическое осаждение из паровой фазы [20], золь-гель метод [21], метод пиролизного распыления [22], метод твердофазной реакции [23] и гидротермальный метод. [24]. Авторы пришли к выводу что, гидротермальный метод является довольно простым и подходящим для промышленного производства, которое позволит разработать недорогой практический газовый датчик для обнаружения вероятных химических агентов. В частности, гидротермальный метод рассматривается как привлекательный процесс получения легированного Eu ZnO из-за простоты, низкой стоимости, возможности массового производства и экологичности. Тем не менее, есть несколько сообщений о ZnO:Eu в виде белого порошка. В этой работе ZnO, легированный Eu, синтезируют с использованием гидротермального метода. Обсуждаются подробные исследования влияния легирования Eu на морфологических и кристаллических структурах синтезированных свойств ZnO и механизм переноса энергии.

В работе [25] изучены структура, морфология и люминесцентные свойства наночастиц ZnO, легированных европием (Eu^{3+}) (NP), подготовленные методом соосаждения. При возбуждении с использованием 325 нм He-Cd-лазера нелегированные наночастицы ZnO демонстрировали слабо известную ультрафиолетовую экситонную рекомбинационную эмиссию (при ~ 384 нм) и сильно широкополосные видимые излучения, связанные с дефектами (при ~ 600 нм). Кроме того, наночастицы ZnO обладали зеленым излучением при ~ 600 нм, связанным с

дефектами, при возбуждении с использованием монохроматизированной ксеноновой лампы. В данном исследовании механизм обменного взаимодействия определена как причина концентрационного тушения люминесценции наночастиц ZnO, легированных Eu^{3+} .

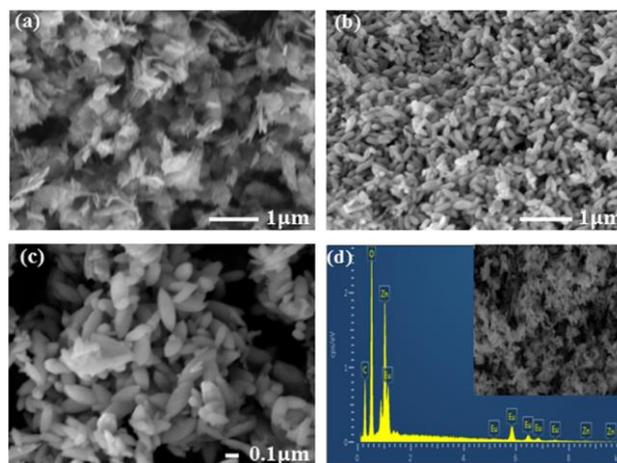


Рисунок 1. Микрофотографии FE-SEM (а) нелегированный ZnO, (б) низкое и (в) высокое увеличение 1,0 мол.% Eu^{3+} , легированного ZnO, и (д) EDS анализ 1,0 мол.% Eu^{3+} , легированных наночастицами ZnO

В работе [26] пленки ZnO, легированные Er и Eu, формировались методом реактивного магнетронного распыления из цинковой мишени с добавками солей Er и Eu. Соотношение содержания цинка и РЗМ выбиралось таким образом, чтобы осаждаемая ZnO пленка содержала 0,7 ат.% – 1 ат.% Er. Распыление производилось в среде аргона с добавлением 20% кислорода. В качестве подложек использовались КЭФ-0,5 и КДБ-1. После синтеза проводились термические отжиги на воздухе в температурном диапазоне $300^\circ\text{C} - 900^\circ\text{C}$.

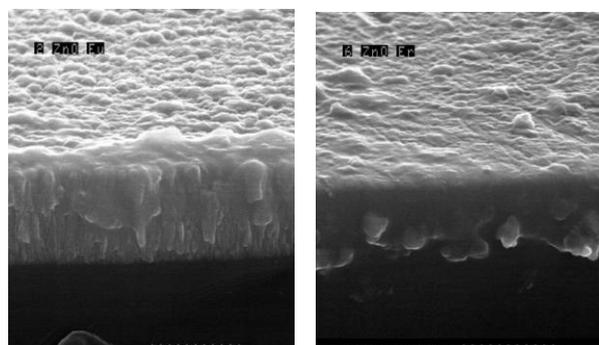


Рисунок 2. Изображения поперечного сечения образцов ZnO:Eu (а) ZnO:Er (б) на кремниевой подложке, полученные сканирующей электронной микроскопией

Изображения поперечного сечения пленок ZnO, легированных РЗМ, полученные сканирующей электронной микроскопией, представлены на рисунке 2. Как видно из рисунка, пленки ZnO, легированные Ег, представляют собой плотно упакованные структуры с практически гладкой поверхностью и размерами зерен ~ 0,1 мкм – 0,15 мкм. В то же

время для пленок ZnO, легированных Ег, характерны большие зерна с размерами в области ~ 0,1 мкм – 0,3 мкм, что сравнимо с толщиной пленки. Таким образом, методом магнетронного напыления получены качественные полупроводниковые слои оксида цинка с плотной упаковкой кристаллитов.

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Сирек кездесетін элементтермен байланған мырыш оксидінің майда дисперсті формаларын синтездеу (шолу)

Кемелбекова А.Е., Мухамедшина Д.М.

Түйіндеме. Берілген мақалада сирек кездесетін элементтері бар мырыш оксидінің жоғары дисперсті формаларын алу әдістері жайлы әдебиеттерден мәліметтер жинақталған. Мырыш оксидін сирек кездесетін жерлік металдармен және 4d өтпелі элементтерімен легирлеу нәтижесінде ZnO жүйелерінің оптикалық қасиеттерін арттыру мүмкіндігі туады. Сонымен қатар, бұл жүйелер 4f және 4d электрондарына берілетін магниттік моментіне байланысты өздерінің ферромагнетизм қасиетіне ие болуы мүмкін. Металл / оксид композиттерінде ZnO қолдану мақсатында жасалған авторлардың зерттеулері бойынша: әр түрлі технологиялық әдістермен алынған сирек жерлік металдармен легирленген мырыш оксиді зерттелген. Сипатталған құрылымдарды алу, жұқа төсеніштердің өсуіне арналған ең жақсы технологиялық параметрлерді таңдау жұмыстары жүргізілді. Нанотехнологияның дамуына байланысты сирек жерлік металды қосылыстары пайдалану бұрынғыдан да танымал бола бастады және нанолуминофорларды, жұқа төсеніштерді, микроорганикалық мембраналарды және золь-гель көзілдіріктерін шығару үшін қолданылатыны көрсетілді.

Түйінді сөздер: мырыш оксиді, сирек кездесетін элементтер, люминафор, CVD әдісі, гидротермальды әдіс, микроұнтақ.

Synthesis of finely dispersed forms of zinc oxide doped with rare-earth elements (review)

Kemelbekova A.E., Mukhamedshina D.M.

Abstract. The paper summarizes the literature data, considers methods for producing highly dispersed forms of zinc oxide doped with rare earth elements. Alloying ZnO with rare earths and 4d transition elements is a popular method of manipulating the optical properties of ZnO systems. These systems may also have their own ferromagnetism due to their magnetic moment transmitted to 4f and 4d electrons. Investigations of authors in this field with the aim of using ZnO in metal / oxide composites are also described: the properties of zinc oxide doped REM powders obtained by various technological methods are studied. We studied the work on obtaining the described structures, the selection of the best technological parameters for the growth of thin films. In connection with the development of nanotechnology, REE compounds have become even more popular and are used to produce nanoluminophores, thin films, microporous membranes, and sol-gel glasses.

Keywords: zinc oxide, rare earth elements, phosphors, CVD method, hydrothermal method, micropowder.

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Synthesis and characterization of vinyl acetate graft copolymers

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Abstract. Graft copolymer P(mPEG-g-VAc) have been prepared by the graft polymerization with a different ratios of mPEG with Mn=2000 macromonomers and Vinyl acetate VAc in the presence of benzoyl peroxide as an initiator using a macro radical initiator technique under influence of heating in toluene has been observed. The graft copolymer P(mPEG-g-VAc) thus formed was characterized with scanning electron microscope SEM, nuclear magnetic resonance ¹H NMR, ¹³C NMR, differential scanning calorimeter DSC, thermo gravimetric analyzer TGA and Fourier transform infrared FT-IR techniques. The results of characterization techniques shows formation of copolymer P(mPEG-g-VAc) while the optimum condition among the studied parameters were as follows; monomer concentration 0.4 mole L⁻¹, ratio (10:90), reaction temperature is 60-85 °C and reaction time is 3 h.

Keywords: polyethylene glycol methyl ether, vinyl acetate, free radical polymerization, catalyst, characterization.

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Introduction

Graft copolymerization is the process in which monomers are bonded to starch backbone through strong covalent bonds. Graft copolymers also exhibit good phase separation and are used for a variety of applications, such as thermoplastic elastomers, compatibilizers, concrete additives, polymeric emulsifiers and surfactants. Due to their branched structure, they melt easily and have potential to achieve a new field of application because of their structures, which is advantageous for processing. [1-5, 13-16].

In addition to other complex polymer systems comprised of star, block, and dendritic architectures, graft copolymer synthesis is an important aspect of polymer science, which continues to receive considerable attention. Graft copolymers can be described as having the general structure 1, where the main polymer backbone A, commonly referred

to as the trunk polymer, has branches of polymer chain B emanating from different points along its length. The common nomenclature used to describe structure 1, where polymer A is grafted with polymer B, is A-graft-B, which can be further abbreviated as A-g-B. Graft copolymers have a variety of potential applications resulting from the wide range of properties available when different polymer chains are connected to form a hybrid branched macromolecule [2].

Many authors [6–8] have distinguished chemical modification of mPEG via graft copolymerization. Much of their work has focused on the synthesis and copolymerization of mPEG macro monomers using anionic, cationic, free radical, and condensation polymerizations, depending on the type of monomer used to prepare the macro monomer.

In this paper the graft copolymer P(mPEG-g-VAc) thus formed was characterized with FT-IR,

^1H NMR, ^{13}C NMR, DSC, TGA, SEM techniques and shown in Figures 1-7.

2 Experimental

2.1 Materials

Polyethylene glycol methyl ether or methoxy poly(ethylene glycol) mPEG, $M_n=2000$, Toluene (ACS reagent, reagent grade >99.7 %) and Hexane (HPLC) were purchased from Sigma Aldrich. Vinyl acetate (99 % stabilized, nitrogen flushed) was purchased from Acros Organics. Dibenzoyl peroxide, 97% (dry wt.), wet with 25% water was purchased from Alfa Aesar.

2.2 Preparation of grafted copolymer P(mPEG-g-VAc)

Firstly, 5 g of mPEG was dissolved in 100 mL of toluene and charged into a 250 mL three-necked reaction flask equipped with a reflux condenser, dropping funnel and thermometer. The reaction flask was involved in a water bath (with automatic temperature control) with settled temperature $60\text{ }^\circ\text{C}$. Benzoyl peroxide (0.1 % weight mass of mPEG) was added to the mixture and heated to $60\text{ }^\circ\text{C}$ under reflux condition. The recrystallization of benzoyl peroxide carried out, dried in an oven at less than $40\text{ }^\circ\text{C}$ and then in desiccator over silica gel to remove water content. In second step, the monomer vinyl acetate (VAc) was fed to the system drop-wise for 40 minutes at $60\text{ }^\circ\text{C}$.

2.3 Mechanism of grafting polymerization

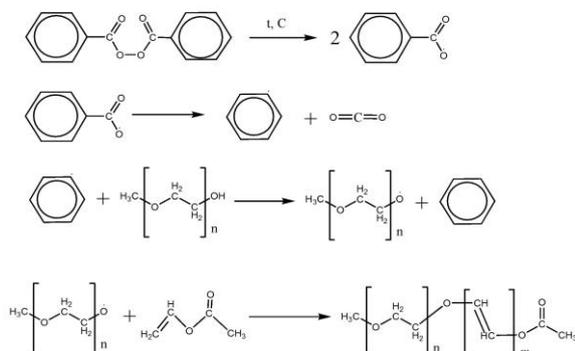


Figure 1 Mechanism of the polymerization

The mechanism of free radical graft polymerization is shown (Fig. 1), and in the step I and II going homolytic dissociation of compounds

such as benzoyl peroxide using heat, that causes the initiation of reaction. In Step III, free radical combines with the trunk polymer and provide a site to attach the Vinyl acetate (VAc) monomer which is provide attaching on the main polymer backbone. Step III is the major step in the synthesis for obtaining the desired copolymer in step IV.

3 Characterization

3.1 Fourier-transform infrared spectroscopy

The samples were characterized by recording the IR spectra of mPEG and P(mPEG-g-VAc) using a Fourier-Transform Infrared Spectroscopy (FTIR) within the wave number range of $4000\text{--}600\text{ cm}^{-1}$ and 32 scans at room temperature. These spectra were measured with a Bruker model Alpha infrared spectrophotometer equipped with diamond crystal.

3.2 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectra (^1H and ^{13}C) of grafted copolymer P(mPEG-g-VAc) were recorded on a Bruker Avance spectrometer at 300 MHz. The spectra were recorded in acetone- d_6 solvent at room temperature ($T = 298\text{ K}$) using acetone residual peak ($\delta = 2.5\text{ ppm}$) as internal reference. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in hertz (Hz).

3.3 Thermogravimetric analysis and Differential Scanning Calorimetry analysis

The thermogravimetric analysis (TGA) of mPEG and its grafted copolymer was carried out with thermo-gravimetric analyzer Mettler Toledo Stare System while Differential Scanning Calorimetry (DSC) by differential scanning calorimeter mettler toledo stare system. The samples were subjected to a constant heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Thermal studies were performed over a temperature range of $30\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ in case of TGA. In DSC studies, the changes in the samples were recorded up to a temperature of $100\text{ }^\circ\text{C}$ i.e. heating from $-50\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$.

3.4 Scanning electron microscopy

The mPEG and grafted copolymer P(mPEG-g-VAc) were characterized by using the microscopic methods to provide information about morphology

of obtained samples. The Scanning Electron Microscopy (SEM) analysis was made by scanning electron spectroscopy (XHR-FESEM) model FEI Verios 460L. Samples were coated with thin layer of gold and examined by electron probe micro analyzer at 5 KV.

4 Results and discussion

4.1 Fourier-transform infrared spectroscopy studies

The FTIR spectra of mPEG and copolymer P(mPEG-g-VAc) are shown in Fig 2. In the spectrum of mPEG, the -C-O-C- and -CH₂- stretching peaks were observed at 1113 and 2880 cm⁻¹. The FT-IR spectra showing typical peaks for C=C at 1634cm⁻¹, C=O at 1735cm⁻¹ and C-O-C at 1099 cm⁻¹, O-CH₃ at 1466 cm⁻¹ are in agreement with the structural characteristics of mPEG-g-VAc. After the formation of grafted copolymer the peaks at 1735 cm⁻¹ and 2886 are due to carbonyl group and C-H bond respectively. Furthermore, C-O stretching at 1241 and 1280 cm⁻¹ is also present. Vinyl group =C-O-C- stretching at 1234 and 1341 cm⁻¹ is also present. The increment in the peak intensity in case of -C-O-C-, the reduction for -OH and presence of carbonyl group peaks in the spectra of grafted copolymer confirm the synthesis of copolymer P(mPEG-g-VAc).

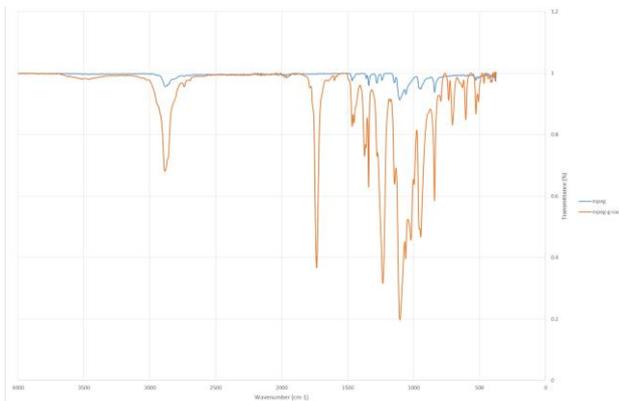


Figure 2 IR spectra of mPEG and copolymer P(mPEG-g-VAc)

4.2 ¹H and ¹³C NMR studies

To obtain more evidence for the synthesized material, the ¹H and ¹³C NMR studies also carried out and the results are shown in Fig 3 and Fig 4 respectively.

Various peaks can be seen for mPEG-g-VAc in Fig 3 with different values of chemical shift.

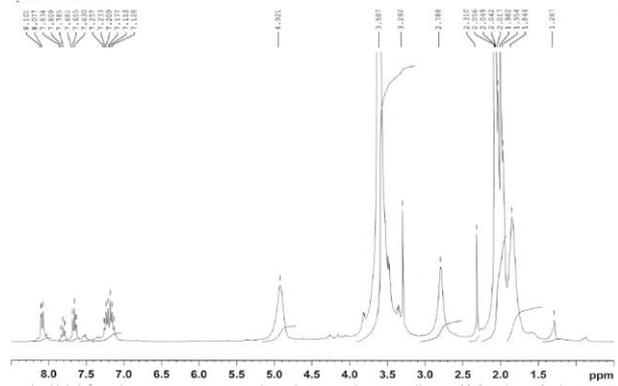


Figure 3 ¹H NMR spectrum of the obtained copolymer P(mPEG-g-VAc)

These values of chemical are assigning on the synthesized copolymer structure as shown in inset. The value of chemical shift for H-C(1) was δ = 3.40 and 3.70 ppm, for H-C(2) δ = 3.54, 3.55 and 3.83, for H-C(3) δ =1.12, for H-C(4) was δ = 2.63 correspond to the protons bonded to C-1, C-2, C-3, C-4 respectively. The ¹H NMR spectra also showed the typical signals attributed to vinyl acetate (4.5 and 5.2 ppm), methyl groups (-CH₃) (1.9 ppm), methylene group (-CH₂) (3.6 and 4.1 ppm).

For obtaining the ¹³C-NMR spectrum of P(mPEG-g-VAc), it was dissolved in acetone and analyzed. The ¹³C NMR spectroscopic data of copolymers P(mPEG-g-VAc) as shown in Fig 4, suggested a molecular formula of C₇H₁₂O₄. The ¹³C NMR spectroscopic data displayed 8 carbon signals, including 3 methyls, 1 secondary, 1 tertiary carbon and 3 carbon signals for acetone. A broad O-H stretching absorption in the region of 1500–1700 cm⁻¹ is ascribable to a carbonyl group, which was evidenced by the carbon resonance. Table 1 also show the value of chemical shift in copolymer P(mPEG-g-VAc) for each carbon.

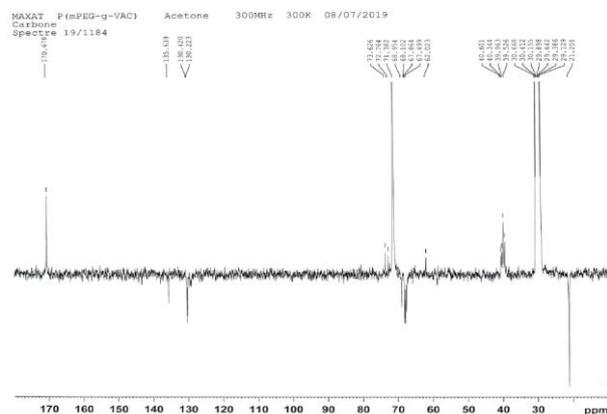


Figure 4 ¹³C NMR spectrum of the obtained copolymer P(mPEG-g-VAc)

4.3 Differential Scanning Calorimetry analysis

The Differential Scanning Calorimetry (DSC) data's of the initial mPEG and obtained copolymer P(mPEG-g-VAc) are shown in Fig 5. The glass transition temperature of copolymer is determined by the chemical composition and structure of their chain and is not a rigidly defined value, as the transition to a glass-shaped state usually occurs in a fairly wide temperature range. Fig 5 shows that the T_g moves toward the low temperatures in mPEG-g-VAc, the value of T_g in pure mPEG is 58.18 °C and in copolymer mPEG-g-VAc it is not defined. In the area of small values of polymer molecular mass, when it passes from glassy to viscous, the glass transition temperature increases with the growth of molecular mass. As soon as the molecular mass reaches the value of the molecular mass of the statistical segment of the macromolecule, the glass transition temperature is virtually independent of the molecular mass [9, 10].

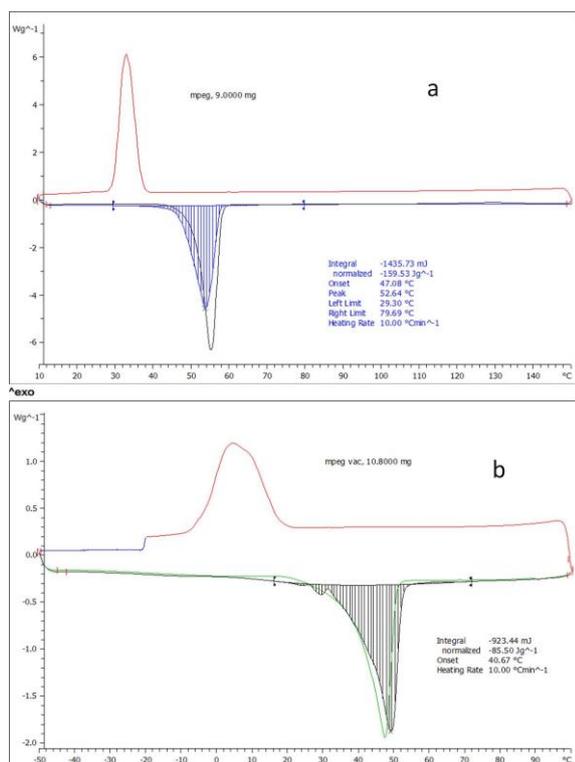


Figure 5 DSC thermograms of mPEG (a) and copolymer P(mPEG-g-VAc) (b)

Melting temperatures (T_m) and enthalpies (ΔH_m) determined by DSC on the second heating scan at heating rates of 10 °C•min⁻¹.

Glass-transition temperature (T_g) taken as the inflection point of the second heating DSC curves recorded at 10 °C•min⁻¹.

Table 1 Thermal properties of mPEG and grafted polymer.

Polymer	DSC analysis			TGA analysis	
	T_m , °C	ΔH , kJ/mol	T_g , °C	T_i , °C	T_{max} , °C
mPEG	47.08	5.7	-		270/405
P(mPEG-g-VAc)	40.67	2.6	-		390/525

4.4 Thermogravimetric analysis

Thermogravimetric Analysis (TGA) of methoxy poly(ethylene glycol) mPEG and copolymer P(mPEG-g-VAc) are shown in the Fig 6. In case of mPEG, the temperature range was between 30 °C and 200 °C and it shows about 99.992 % loss in weight that can be seen in Fig 6 and Table 1. This may be corresponding to the degradation of pure mPEG.

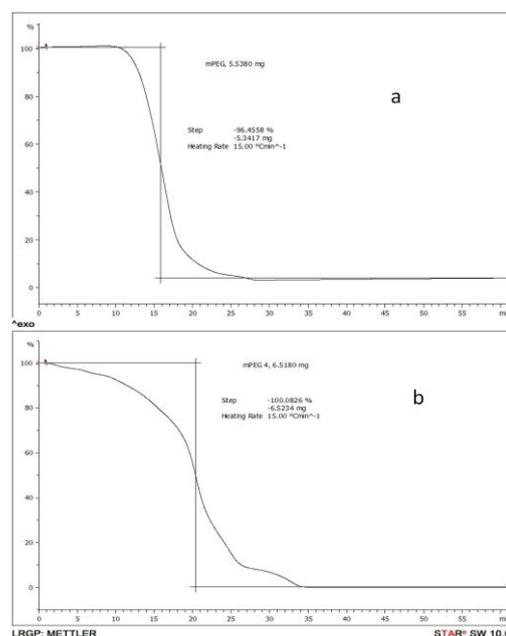


Figure 6 TGA thermograms of mPEG (a) and copolymer P(mPEG-g-VAc) (b)

The TGA of the copolymer P(mPEG-g-VAc) shown in Fig. 6 reflect two stages of weight loss between 30 and 200 °C (Table 2). In the first stage, the temperature range was between 30 and 120 °C with the loss of about 18 % due to the impurities. The second stage of weight loss starts at 120 °C and continues to 200 °C, corresponding weight loss of about 82 % due the weight losses of heating promote decomposition process of P(mPEG-g-VAc). This proves that grafted copolymer has excellent thermal stability and it can be widely used for different applications. Block copolymers also

show semicrystalline character with T_m between 44 °C and 56 °C and superior melting enthalpies for those with longer mPEG. Unlike PDHU, block copolymer do not show detectable T_g s. Concerning grafted polymers they are amorphous with low T_g s indicating that grafting mPEG groups prevent crystallization of aliphatic polymer chains. Thermal stability evaluated by TGA shows scarce differences between the homopolymer and its corresponding block copolymers. Different behavior was observed for grafted polymers with a significant decrease in temperature at which 5% weight loss takes place although temperature for maximum degradation rates are similar. This could be related to the higher percentage of labile ester groups and their lower molecular weight [11].

Block or graft copolymers can be self-assembled to form micelles in their selective solvents. Compared with linear block copolymers, graft copolymer can add considerable functionalities on the branched chains with great advantage of convenient chemical modifications in advance of the self-assembly process [12].

4.5 Scanning electron microscopy

The scanning electron micrographs of pure mPEG and copolymer P(mPEG-g-VAc) are shown in Fig 7.

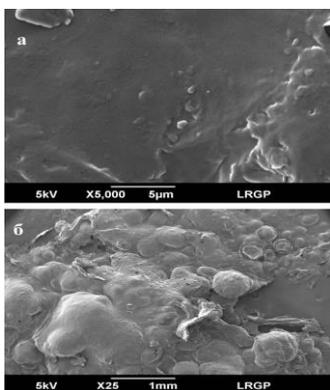


Figure 7 Results of pure mPEG (a) and copolymer P(mPEG-g-VAc) (b) on scanning electron microscope (Mag = 5000)

The SEM image of mPEG shows a smooth surface, because there is a stronger interaction between mPEG molecules. On the other hand, the SEM images of copolymer P(mPEG-g-VAc) prove the uniform distribution of VAc. The graft copolymerization of VAc modified the surface morphology of mPEG and homogenous grafted copolymers P(mPEG-g-VAc) was obtained.

Conclusions

The graft copolymer P(mPEG-g-VAc) was successfully synthesized using benzoyl peroxide as an initiator by free radical polymerization method. The characterization was performed using various techniques such as FT-IR, SEM, nuclear magnetic resonance (^1H NMR, ^{13}C NMR), DSC, and TGA. The obtained results from this experiments revealed that the optimum conditions for grafting copolymer P(mPEG-g-VAc) were found as follows: ratio is 10:90, monomer concentration 0.42 mol/L, reaction temperature is 60-85 °C and reaction time is 3 h. NMR study confirmed that all the groups present in the copolymers. The results of the thermal stability show that grafted copolymer has excellent thermal stability and it can be widely used for different applications. Moreover, the rate of decomposition is highly improved through grafting and through polymerization of the grafted samples. Therefore, this copolymer can be used for various applications including surfactant in chemical technology.

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Винилацетатты полимерлердин синтезі мен сипаттамасы

Мырзаханов М.М., Эль Сайд Негим, Мохамад Насыр

Түйіндеме. Полиэтилен гликольді метил эфирі $M_n = 2000$ макромономері мен винил ацетат мономері VAc бос радикалды полимерлеу арқылы алынған сополимер P (mPEG-g-VAc), катализатор ретінде бензойл пероксиді және қыздыру әсерінен алынды. Осылайша пайда болған сополимер P (mPEG-g-VAc) сканерлеуші электронды микроскоппен (SEM), 1H , ^{13}C ЯМР спектрометрімен, дифференциалды сканерлеу калориметрімен ДСК, ТГА термогравиметрімен және инфра қызыл-Фурье спектрометрімен сипатталды. P (mPEG-g-VAc) сополимернің сипаттамасының нәтижесінде синтезді жүргізудің оптимальді параметрлері анықталды: мономер концентрациясы $0,4 \text{ моль л}^{-1}$, бастапқы заттардың қатынасы (10:90), температура реакциясы $60-85 \text{ }^\circ\text{C}$, және синтез уақыты 3 сағат.

Түйінді сөздер: полиэтиленгликоль метил эфирі, винил ацетаты, бос радикалды полимеризация, катализатор, сипаттама.

Синтез и характеристика винилацетатных прививочных полимеров

Мырзаханов М.М., Эль Сайд Негим, Мохамад Насыр

Аннотация. Сополимер P(mPEG-g-VAc) был получен путем прививочной полимеризации с различными соотношениями полиэтиленгликоль метилового эфира mPEG с $M_n=2000$ макромономеров с винилацетатным мономером VAc в присутствии перекиси бензоила в качестве инициатора с использованием метода макрорадикального инициатора под воздействием нагрева в толуоле. Образовавшийся таким образом сополимер P(mPEG-g-VAc) был охарактеризован сканирующим электронным микроскопом СЭМ, 1H , ^{13}C ЯМР-спектрометром, дифференциальным сканирующим калориметром ДСК, термогравиметром ТГА и спектрометром ИК-Фурье. Результаты методов характеризации показывают образование сополимера P (mPEG-g-VAc), в то время как оптимальные условия среди изученных параметров были следующими; концентрация мономера $0,4 \text{ моль л}^{-1}$, соотношение (10:90), температура реакции составляет $60-85 \text{ }^\circ\text{C}$, и время реакции составляет 3 часа.

Ключевые слова: полиэтиленгликоль метиловый эфир, винил ацетат, свободнорадикальная полимеризация, катализатор, характеристика.

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Disposal of slag of refined ferrochromium by obtaining a sintered and carbonized construction products

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Abstract. The article investigates the material composition of refined ferrochromium slag. It has been confirmed that the main compound in the slag is dicalcium silicate. The disposal problem of self-disintegration slag in the current production of refined ferrochromium can be solved by controlling its basic capacity with obtaining stabilized lump slag that is not influenced to silicate decomposition. This became the basis to researches the production of non-disintegrating burnt construction products from slags using low-melting silica-containing additives that reduce the slag basicity. Briquettes roasting containing from 20 to 30% additives in the temperature range of 1200-1225 °C showed the possibility of obtaining ceramic construction products. Material analysis of the slag also showed that the slag components, such as calcium oxide and magnesium oxide, are compounds prone to the formation of carbonates, which leads to the setting between the slag particles. Which makes it possible to obtain construction products in the process of autoclaving processing of bricks from the slag in the carbon dioxide environment. The influence of fineness, slag moisture, and the dwell time of products in an autoclave in the carbon dioxide environment on the strength of the resulting pellets were evaluated in this paper. It was determined that moderate humidity, in addition to increasing ductility during pellet molding, also increases the strength of products after carbonization. Excessive grinding of slag negatively affected on the quality of the pellets. The increase in compression force during the pellets formation, on the contrary, increased the strength of the products. An increase in the duration of carbonization at constant pressure had a positive effect on the strength increase of pellets.

Keywords: self-disintegration slag, recycling, construction products, sintering, carbonization.

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Introduction

The accumulation of man-made wastes in the traditional metallurgical regions leads to increasingly negative consequences, both for the natural environment and for economic indicators of production. Dusting, soil and wastewater pollution with heavy metals, covering vast areas,

environmental charges paid by the plants and their annual increase, these are some of the negative aspects of the disposal and storage of production wastes.

The main scopes of accumulated man-made mineral formations of only ferroalloy plants in the Ural mountain region are represented by the slag dumps of the Aktobe plant (14 million of tons of

ferrochromium slag). Serov ferroalloy plant is 6.61 million of tons of ferrochromium slag. Klyuchevsky ferroalloy plant is 5,75 million of tons of slag and the Chelyabinsk Electrometallurgical Plant the slag production of low-carbon ferrochromium is 8.2, carbon and conversion ferrochromium is 3.3, ferrosilicon and ferrochromium silicon is 1.0, ferro-tungsten is 0.53, ferromolybdenum is 0.5 million tons [1, 20-22]. The most problematic of them are self-scattering slags. This type of slag disposal is still a big problem that has not found practical solution in industrial scopes. Among these slags, a separate species can distinguish self-decaying slag from the production of refined ferrochromium (hereinafter - RFC).

At the same time, with the development of engineering and technology, the processing of accumulated wastes becomes more accessible and profitable. Ferroalloy slag is a good raw material for metal concentrate production. In addition, during processing, you can get other materials that can be used as raw materials, for example in the construction industry.

Main part

At the same time, with the development of engineering and technology, the processing of accumulated wastes becomes more accessible and profitable. Ferroalloy slag is a good raw material for metal concentrate production. In addition, during processing, you can get other materials that can be used as raw materials, for example in the construction industry.

In the current production, the problem of RFC slag disposal is solved by their stabilization in the alloy smelting process to produce non-crumbling lump slags. Compounds of magnesium, iron, phosphorus, barium, aluminum and boron have a stabilizing effect. To date, the most common stabilizers are boron compounds, which is due to the small amount of additives to obtain stabilized slag [2, 3, 4]. Another method for stabilizing slag is to change the basicity of slag to 1.3-1.4 values or more than 3.2 [5, 6].

In the paper, the chemical composition of the slag of ferrochromium-refined grades was studied (Table 1).

Table 1 Chemical analysis of refined ferrochromium slag, %

Cr ₂ O ₃	SiO ₂	MgO	FeO	CaO	Al ₂ O ₃
6*	26	12	2	48	6

* - in terms of total chromium to oxide

The metal chromium content is on average about 2%.

The composition of the slag from the slag dump according to x-ray phase analysis are given in Table 2.

As the data provide about the slag composition, its use as a raw material for cement production is

hindered by the high content of free periclase and the dicalcium silicate availability, which is confirmed by published data [7].

To determine the stabilization capacity by reducing the basicity, calculations were performed to determine the equilibrium phase composition of the six-component Cr₂O₃-SiO₂-Al₂O₃-FeO-CaO-MgO system based on the chemical composition of the natural slags. The calculation was carried out using a software package worked out by HMI named after J. Abishev [8]. The basicity was varied by increasing / decreasing the fraction of silica in the composition with an unchanged amount of the remaining components of the slag. Based on the results of calculating the equilibrium phase composition of the system, the dependence of the change in the content of 2CaO·SiO₂ in the slag on the change in the basicity of the slag is shown in Figure 1. The diagram shows that there are two regions in the system in which dicalcium silicate is substantially absent with a basicity of less than 1.4 and more than 3.2.

Table 2 Material composition of the slag of refined ferrochromium production

Formula	Percentage, %
Ca ₂ (SiO ₄)	33.2
MgFeAlO ₄	22.5
Ca ₃ Mg(SiO ₄) ₂	20.5
CaAl ₂ SiO ₆	7.9
MgO	6.5
Ca ₂ SiO ₄	5.9
Fe ₂ O ₃	3.5

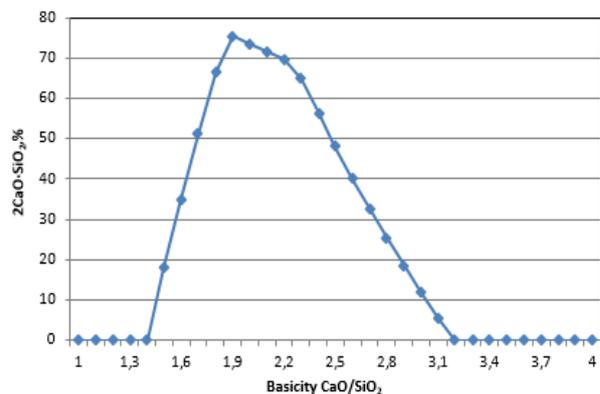


Figure 1 Change in the 2CaO·SiO₂ content in the slag depending on basicity

To stabilize RFC slag as regards technology is more efficient by reducing the basicity to less than 1.3 values, since slag with a basicity of more than 3.2, where tricalcium silicate is the main phase, have a high melting point. RFC slag with a basicity of less

than 1.3 as concerns physical properties are similar to raw materials for the ceramic products manufacturing.

The practical goal of this part of the work is to develop the composition of ceramic products with a base from stabilized by sintering RFC slag with reduced basicity obtained from raw materials kempirsay ore massif. Ceramic products in industry are obtained by firing molded products from various clays. Firing products is usually carried out at a temperature of 900-1000 °C. Fire-resistant and high-melting clays have a large sintering interval (more than 100 °C) and are used to obtain products with a dense sintered shard; burn them at 1150 ... 1400 °C. For firing ceramic materials use special furnaces (ring, tunnel, slot, roller, etc.) [9].

The current RFC slags, having a ~ 1.9 basicity, contains about 75% of $2\text{CaO}\cdot\text{SiO}_2$ and corresponds to the maximum of the curve in Figure 1. Therefore, any change in basicity leads to a decrease in the content of $2\text{CaO}\cdot\text{SiO}_2$. In this paper, non-deficient silica-

containing materials with a relatively low melting point (not higher than 1300 °C) - expanded clay (hereinafter – Clay 1) and clay of kempirsay ore massif (hereinafter – Clay 2), as well as ground natural crushed stone (hereinafter – Breakstone) were considered as stabilizing additives. The average chemical composition of these materials is presented in Table 3.

To obtain basicity below a 1.4 value, the least additive component of stabilizing additives is estimated. When using Clay 1, it should be at least 15%, Clay 2 - 17.5%, Breakstone - 22%.

The sintering temperature of the RFC slag itself is above 1500 °C; however, the addition of these components significantly reduces this temperature. Correspondingly, in the state diagrams of $\text{SiO}_2\text{-CaO-MgO}$ and $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$, with the inclusion of the above additives in an amount of 15-45%, the melting temperature of the system will lie in the range of 1320 - 1400 °C. In this regard, the studies of the sintering process were carried out in the range of 1000 - 1250 °C.

Table 3 The chemical composition of stabilizing additives, mass. %

Item	CaO	SiO ₂	MgO	Al ₂ O ₃	Cr ₂ O ₃	FeO	C	S	LOI
Clay 1	1.6	60.8	2.5	16.9	1.4	8.1	1.0	0.6	7.0
Clay 2	6.9	58.5	2.8	12.4	-	6.4	-	0.2	12.8
Breakstone	9.7	51.4	4.9	14.3	0.2	13.8	-	0.01	5.7

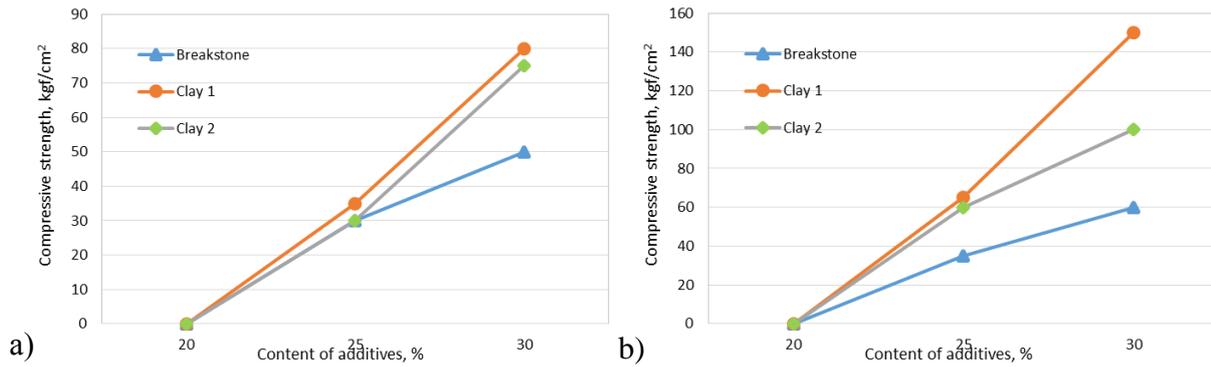
The materials used were pre-dried and ground for the researches. The moistened mixture of the slag and stabilizing additives was subjected to semi-dry pelleting (+15% of water over dry weight) with a compression force of 3 kN / cm². The pellets had a rectangular shape with a dimension of 50 × 50 × 30 mm. The firing was carried out in an electric muffle furnace; the heating time of the samples was 8-10 hours, exposure at a maximum temperature of 3-5 hours, cooling along with the furnace for 12-14 hours.

Previous experiments made in the laboratory regarding stabilizing RFC slag by adding silica-containing materials by fusing them showed that their addition in the minimum amount required did not ensure stabilization of the samples in the entire volume. A 20% increase in the amount of stabilizing additive allowed the slag to be completely stabilized. Given this feature of the process, the share of the stabilizer in the mixture was set to at least 20%.

No sintering was observed in the temperature range of 1000–1150 °C; pellets scattered with minimal physical impact. Strength values did not exceed 8 kgf / cm².

Pellets sintering occurred at a temperature of 1200 and 1225 °C. Studies were carried out with the addition of stabilizers in the slag in the amount of 20, 25 and 30%. The results of testing sintered pellets for compressive strength are provided in Figure 2.

As Figure 2 provides, sintering with the content of stabilizer additives in 20% sintering did not occur. An increase in the additive content up to 25% at a temperature of 1200 °C leads to sintering of pellets. While strength indicators are obtained that are in the range of 30-35 kgf / cm² for all types of stabilizers, an increase in firing temperature to 1225 °C increases this value for expanded Clay 1 by 85% (65 kgf / cm²), for Clay 2 100% (60 kgf / cm²), and for Breakstone it remains unchanged (30 kgf / cm²). Pellets containing 30% additives showed an increase in strength compared to 25% at 1200 °C for Clay 1, Clay 2 and Breakstone at 1200 °C by 130% (80 kgf / cm²), 150% (75 kgf / cm²) and 67% (50 kgf / cm²) respectively. The same content of additives at 1225 °C showed an increase in strength by 330% (150 kgf / cm²), 230% (100 kgf / cm²) and 100% (60 kgf / cm²), respectively.



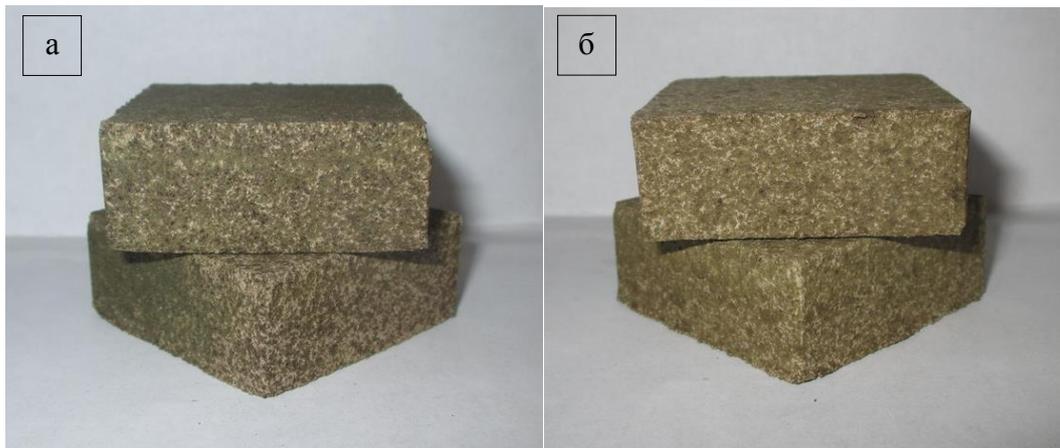
a – 1200 °C, b – 1225 °C

Figure 2 Compressive strength during sintering of slag with stabilizing additives

A significant increase in strength occurs with a content of 30% stabilizing additives and firing at a temperature of 1225 °C. A further increase in the firing temperature (≥ 1250 °C) leads to the appearance of cracks on the surface and deformation of the pellets. Figure 3 demonstrates samples of sintered pellets.

In [10], studies were carried out to determine the ceramic properties of various metallurgical slags

with the addition of a clay component. Ceramic products with a compressive strength of 200 to 400 kgf / cm² were obtained. The sintering temperature was in the range of 1150 - 1350 °C. In [11], it was proposed to obtain porous pellets from a mixture of slag, diatomite, and sodium silicate solution, sintered aggregates for concrete sintered at 1050 °C.



a - with the addition of Clay 1; б - with the addition of Clay 2

Figure 3 Samples of sintered pellets from RFC slag

Another way to utilize RFC slag can be the method of obtaining high-strength building products by autoclave carbonization. Given the high content of calcium and magnesium oxides in the slag, it has a high tendency to form carbonates [12]. Similar work on the use of slag from steelmaking, having a similar chemical and mineral composition, indicates the possibility of carbonization of self-dissolving slag with obtaining agglomerated products of high strength [13, 14, 15].

It is clear that metal carbonates are formed by exothermic reactions of the where MeO is a divalent metal oxide.



With increasing pressure of carbon dioxide in the MeO-CO₂-MeCO₃ system, the affinity of MeO to CO₂ increases, and the carbonization reaction proceeds with the release of heat. Carbonization occurs most intensively with a moisture content of 5-8%. It is noted that with complete drying of the material, as well as with its excessive moistening, the process stops or extremely slows down [16, 17].

Based on the above reasoning, we conducted studies on the carbonization of stale slag of refined ferrochromium. For the experiments were used: steel mold with a mesh size of 50 × 50 mm; test press,

hydraulic IP-50; high pressure autoclaves with a volume of 0.7 and 2.0 liters. Food carbon dioxide from cylinders was used as CO₂.

In the conducted experiments, the influence of fineness, moisture of the used slag and the duration of exposure of the products in an autoclave in a carbon dioxide medium to the strength of the resulting pellets was evaluated. Pellets were made similar in shape to sintered pellets. The size of the ground slag from which the pellets were molded: $-1 + 0$ mm; $-0.16 + 0$ mm; $-0.071 + 0$ mm. Humidity: 15%, 8% and 5% over dry weight. Moistening of the material is also required to improve the process of forming briquettes. The pressing force during molding was 1.5 and 3 kN / cm². The pressure in the autoclave in all cases was 10 atmospheres. The exposure time is 12 hours. The quality of the pellets was evaluated by assessing the compressive strength according to GOST 8462-85 on the IP-1000 test press. The results are provided in Table 4.

The data provided make it clear that the moisture content increased to 15% significantly reduced the strength of carbonized products - on average by 37.5% compared with the same samples, but obtained at 5% humidity. Therefore, the remaining experiments were performed at a moisture content of 5% and 8%. In accordance with the known laws of briquetting, the strength of briquettes consisting only of small particles is not high at any humidity and pressing pressure [18]. An increase in the maximum particle size of the used slag significantly increased the strength of the resulting briquettes. The maximum values of compressive strength were obtained with a grain size of $-1 + 0$ mm, a holding time of 12 hours, and a pressing force during molding of 3 kN / cm². For these samples, sieving was carried out in

fractions to determine the particle size distribution. The sieving results are shown in Table 5.

The experiments were carried out according to the best option (material fineness $-1 + 0$ mm, pressing force 3 kN/cm²) with exposure to carbon dioxide for 6, 12, 18 and 24 hours at a pressure of 10 atmospheres to determine the kinetics of the carbonization process. The average values of the obtained strength test results are shown in Figure 4.

As can be seen from this figure, there is an almost linear dependence of the compressive strength of pellets made from stale RFC slag on the time of autoclaving in carbon dioxide. The appearance of pellets after 12 hours of carbonization is shown in Figure 5.

The results make it clear that although the process of carbonization of slag accelerates with increasing fineness of its grinding as stated in [19], nevertheless, the strength of pellets decreases with increasing fineness of grinding. Apparently, this is explained by the fact that in studies [19], the slag was carbonized without preliminary agglomeration. However, in our case, a more optimal particle size distribution (an equal amount of small, medium, and large particles by weight) has a stronger effect on the strength of pellets after carbonization.

It is also noted that in order to achieve maximum strength when working with the same slag, in addition to the particle size distribution, it is necessary to take into account the moisture content of the initial mixture. So, for a mixture with a fineness of $-0.16 + 0$ mm, the effective humidity is lower than in the case of $-1 + 0$ mm, which is apparently due to the different gas permeability of mixtures of different particle size distribution during autoclaving.

Table 4 The pellets strength after carbonization

Items	Fractional composition of used slag, mm					
	$-0.071 + 0$		$-0.16 + 0$		$-1 + 0$	
Relative humidity, %	5	15	5	8	5	8
Strength, kgf / cm ² *	122.2/112.0	84.6/85.3	418.0/349.3	321.4/306.2	309.9/436.2	311.2/357.1

* In the numerator - at a pressing pressure of 1.5 kN / cm², in the denominator - at 3 kN / cm².

Table 5 Granulometric composition of RFC ground slag

Fraction, mm	Mass fraction part, %
>1.0	0.09
>0.63	0.22
>0.4	5.31
>0.2	26.18
>0.1	44.64
>0.063	56.81
<0.063	42.43
Sieving losses	0.76

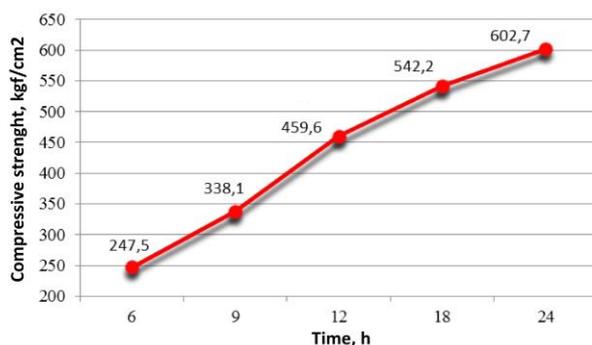


Figure 4 The change in the strength of carbonized pellets depending on the time of autoclaving



Figure 5 Pellets look after carbonization for 12 hours

Findings

Studies conducted have shown the possibility of obtaining building ceramic products from RFC slag with stabilizing additives. The preservation of the structural integrity of the pellets and their high compressive strength are confirmed by theory studies on the stabilization of self-decaying slag by reducing the basicity during sintering. The use of claydite clay and clay of kempirsay ore massif as stabilizers in an amount of at least 30% at a firing temperature of 1225 °C makes it possible to obtain brick grades M150 and M100 (according to State Standard 530-2012), respectively.

The use of ground natural crushed stone as a stabilizer did not allow to raise the strength of products above the values corresponding to the grade of brick M50.

Autoclave carbonization of RFC stale slag in a carbon dioxide environment makes it possible to obtain molded articles with high strength, which can be adjusted due to the autoclave holding time. Molded carbonized products from stale slag of refined ferrochromium are superior in strength to concrete and silicate construction products.

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Тазартылған феррохромның қожын күйдірілген және карбоназацияланған құрылыс бұйымдарды жасау арқылы кәдеге жарату

Сариев Ө.Р., Мусабеков Ж.Б., Досекенов М.С.

Түйіндеме. Мақалада тазартылған феррохром қожының заттық құрамы зерттелген. Қождың негізгі қосындысы қос кальцийлі силикат екендігі дәлелденді. Ағымдағы өндірістегі өздінен ұнтақталатын қождың мәселесін негізділік реттеу арқылы силикаттық ыдырауға ұшырамайтын тұрақтандырылған кесек қож алуға болады. Осының негізінде негізділікті азайтатын оңайбалқығыш кремний тотығы бар қоспалар қолдану арқылы күйдірілген құрылыс бұйымдарды алу тәсілі зерттелді. Құрамында жиырмадан отыз пайызға дейін қоспалары бар

брикеттерді температурасы 1200-1225°C аралығында күйдіру процесі керамикалық құрылыс бұйымдарын алуға мүмкіншілік бар екенін көрсетті. Қождың заттық құрамын зерттеуі кальций және магний тотықтары карбонаттар құруына бейім екендігін көрсетті, соның арқасында қождың түйіршіктері бір-бірімен қосылып қатаюына соқтырады. Карбонизация процесі қождан жасалған кірпіштерді көміртегі қос тотығы ортасында автоклавтық өндеу арқылы өндіруге мүмкіндік береді. Жасалғана зерттеу жұмысында шығарылған брикеттің беріктігіне қождың ірілігі, дымқылдығы және автоклавта ұстау уақытының әсері бағаланды. Ынапты дымқылдық қорамалау кезіндегі созылымдықпен тек көбейтпей сонымен бірге карбонизациядан кейінгі беріктілікті арттыратынын көрсетті. Қождың шамадан тыс ұнтақтануы брикеттердің сапасына кері әсер етті. Қормалау кезіндегі қысу күшінің үдей түсуі бұйымдардың беріктілігіне жақсы әсер етті. Көмірқышқыл газ атмосферасында қысым тұрақты болған жағдайда карбонизация ұзақтығын арттыру брикеттердің беріктігіне оң әсер етті.

Түйін сөздер: Өздігінен ұнтақталатын қож, кәдеге жарату, құрылыс бұйымдары, қақтау, карбонизация.

Утилизация шлака рафинированного феррохрома с получением спечённых и карбонизированных строительных изделий

Сариев О.Р., Мусабеков Ж.Б., Досекенов М.С.

Аннотация. В статье исследован вещественный состав шлаков рафинированного феррохрома. Подтверждено, что основным соединением в шлаке является двухкальциевый силикат. Проблему утилизации саморассыпающегося шлака в текущем производстве рафинированного феррохрома, возможно, решать регулированием его основности с получением стабилизированного не подвергающегося силикатному распаду кускового шлака. Это послужило основой для проведения исследований по получению не распадающихся обожжённых строительных изделий из шлаков с применением легкоплавких кремнезёмсодержащих добавок снижающих основность шлака. Обжиг брикетов, содержащих от 20 до 30 % добавок в температурном интервале 1200-1225°C, показал возможность получения керамических строительных изделий. Вещественный анализ шлака также показал, что компоненты шлака, такие как оксид кальция и оксид магния являются соединениями склонными к образованию карбонатов, что приводит к схватыванию частиц шлака между собой. Также даёт возможность получать строительные изделия в процессе автоклавной обработки кирпичей из шлака в среде углекислого газа. В приведённой работе было оценено влияние крупности, влажности шлака и длительности выдержки изделий в автоклаве в среде углекислого газа на прочность получаемых брикетов. Установлено, что умеренная влажность помимо повышения пластичности при формовке брикетов, также увеличивает прочность изделий после карбонизации. Чрезмерное измельчение шлака негативно сказалось на качестве брикетов. Нарастание усилия сжатия при формовании брикетов наоборот подняло прочность изделий. Увеличение длительности карбонизации при неизменном давлении сказалось положительно на росте прочности брикетов.

Ключевые слова: Саморассыпающиеся шлаки, утилизация, строительные изделия, спекание, карбонизация.

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Silver, gold and palladium leaching from electronic scrap using bromine- bromide solution

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Abstract. This study investigated the thermodynamics and kinetics of gold and accompanying noble metals, such as silver, palladium and platinum, leached from the electronic scrap by bromine-bromide solutions. Theoretical and practical analysis of the behavior of gold in the traditional $\text{Br}_2 - \text{Br}^- - \text{H}_2\text{O}$ system confirmed the fact that in a neutral and slightly acidic medium, when bromine hydrolysis proceeds slightly, a bromine in bromide solution can be used to leach gold. In this case, bromine-bromide leaching compared with cyanidation is more favorable in terms of kinetics and selectivity. In particular, when brominated in a neutral medium as a result of the formation of a passivating copper monovalent copper (Cu_2O) film on the surface of copper particles, copper does not go into solution, while copper forms stable soluble anionic complexes with cyanide. For the first time in order to stabilize the pH in the alkaline area the conditions for gold leaching in the presence of a phosphate buffer solution (NaH_2PO_4) were investigated. The effect of the pH of the leach solution, the concentration of active bromine, bromide ions and the concentration of the buffer solution on the leaching kinetics of gold was studied. It was established experimentally that a noticeable dissolution of gold begins at $\text{pH} \leq 8$, and at pH 6, almost all gold passes into the solution. A sufficient concentration of active bromine under these conditions can be considered $6.6 \text{ g} \cdot \text{dm}^{-3} \text{ Br}_2$ at a bromide concentration of $20 \text{ g} \cdot \text{dm}^{-3} \text{ NaBr}$. Leaching with the productive solution turnover made it possible to reduce the consumption of bromine from 89-95 to 20-32 kg Br_2 per ton of scrap and raise the concentration of gold from 76 to 195 $\text{mg} \cdot \text{dm}^{-3}$. In this paper, it was first shown that silver and palladium in the system under study ($\text{pH} = 5-6$) begin to dissolve noticeably only at high concentrations of bromide ions. Complete dissolution of palladium is achieved with an excess of bromide ions and pH values of 1.5-2.0. Platinum turned out to be more resistant to bromine-bromide leaching because of the formation of a sparingly soluble platinum dibromide on its surface.

Keywords: gold hydrometallurgy, computer scrap, thermodynamics and kinetics of noble metal dissolution with bromine, phosphate buffer solution.

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Introduction

Due to the rapid development of technology and an incredible increase in demand for more advanced electronic devices, the service life of the latter is constantly reduced, which causes an increase in the volume of electronic waste. It is generally accepted that electronic waste is a dismantled electrical and electronic

equipment due to the expired life and not intended for reuse [1-4, 16-17]. E-waste typically includes household electronic appliances, toys, electrical tools, cell phones, monitoring and control instruments, automatic dispensers, IT, telecom equipment and other consumer items. According to data for 2014, about 41.8 million tons of electronic waste was generated in the world, and it is expected that the

amount of electronic waste will reach 49.8 million tons in 2018, and the annual increase will be from four to five percent [1].

Since e-waste has a high content of copper and precious metals, it is a valuable source of copper for the copper smelters.

The current practice of processing PCB (Personal Computer Boards) concentrates using reflective smelting technology at a smelter does not exclude the loss of precious metals with smelting slags [5,6].

Hydrometallurgical approaches make it possible to eliminate the loss of metals during processing and could be less harmful to the environment once the technology is implemented. Therefore, a combined scheme consisting of enrichment and hydrometallurgical processing of printed circuit boards concentrate seems to be in many respects a technical solution with a high potential [2-4].

The content of non-ferrous and precious metals contained in the final concentrate of printed circuit boards depends on the type of source of the electronic equipment, its composition and especially the year of manufacture. It is well known that the older electronic equipment (60-70 years old) contained significantly more precious metals than modern devices do.

The table. 1 presents the results of the standard chemical analyses of representative samples of PCB concentrates taken from the practice of the Israeli company All Recycling Ltd.

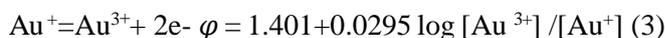
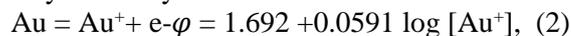
Table 1 - Results of chemical analysis of PCB concentrates

Type	The Results of chemical analysis, wt., %				
	Cu	Ag	Au	Pd	Pt
Rich	17.85	0.126	0.035	0.025	0.0005
Rich	17.51	0.087	0.023	0.017	0.0034
Rich	19.84	0.119	0.031	0.024	-
Reg.	18.19	0.114	0.011	0.010	-
Reg.	18.39	0.136	0.011	0.012	-
Reg.	20.49	0.137	0.006	0.004	0.0003
Poor	26.06	0.052	0.005	0.002	-
Poor	22.46	0.026	0.003	0.002	-

As can be seen from the results of a chemical analysis of ordinary concentrates of printed circuit boards, the general characteristic of PCB concentrates is the multicomponent nature of the raw material, and the content of precious metals varies in the range, wt.,%: Silver (0.026-0.126), gold (0.0034-0.035), palladium (0.0020- 0.025) and platinum (0.00-0.0034)

Their resistance to oxidative leaching distinguishes gold and platinum group metals.

Oxidation of gold in water proceeds with the sequential formation of monovalent Au (I) and trivalent Au (III) ions, which is confirmed thermodynamically:



The dissolution of gold can occur only in the presence of a sufficiently strong oxidizing agent, the electrode potential of which is reduced by the introduction of complexing ligands, for example, the bromide ion.

The study evaluated Br₂ / Br⁻ system as an alternative to cyanide leaching of gold contained in sulfide and in oxidized concentrates. It was shown [7,8] that when leaching gold contained in sulfide concentrates using elemental bromine, significantly higher gold recovery can be achieved than with cyanide, but the consumption of bromine was high due to the simultaneous oxidation of sulfides. The recovery of gold from oxide concentrates by bromine was comparable to that achievable with cyanide, and bromine consumption was reasonable when leaching was carried out at an almost neutral pH of ~ 6. In the case of oxidized gold-bearing ores containing copper mineralization, bromine consumption was lower than cyanide consumption, as the authors of [7] suggested that bromine with copper minerals is less reactive than cyanide.

As our preliminary experiments with electronic scrap showed, a significant leaching of gold is observed at pH ≥ 8, which allows us to maintain selectivity with respect to the main accompanying metals. In this regard, the study of the optimal conditions for the dissolution of gold and related noble metals in the process of bromine-bromide leaching is of practical and theoretical interest.

Thus, the present work is devoted to studying the thermodynamics and kinetics of the dissolution of gold and related valuable metals, mainly copper, silver, palladium and platinum from typical samples of electronic scrap in the bromine-bromide system, depending on the pH of the medium, the concentration of active bromine, bromide ions and phosphate buffer solution.

Experimental part. Devices and reagents

A series of experiments was prepared using a sample of PCB concentrate composition, wt., %: 20.49 Cu, 5.34 Al, 4.39 Sn, 2.02 Al, 1.39 Zn, 3.43 Pb,

1.06 Ni, 0.137Ag, 0.0058 Au, 0.0042 Pd, 0.0003 Pt, pre-shredded using a Retch GmbH laboratory hammer shredder to a particle size of 0.5-2 mm.

The reagents used were HCl (Fluka Israel), HNO₃ (Fluka Israel), NaBr (Fluka Israel), HBr (Fluka Israel), NaH₂PO₄ (Fluka Israel) and concentrated (434 g·dm⁻³) elementary bromine solution manufactured by Bromine Compound. Reagent solutions were prepared using bidistilled water.

Leaching was carried out at 298.5 K, the ratio of the contacting phases T: W = 1: 5 and the speed of rotation of the stirrer 300 rpm. g·dm⁻³. The required amount of leaching solution containing 20 g·dm⁻³ NaBr and 70 g·dm⁻³ NaH₂PO₄·H₂O was poured into a reaction vessel equipped with a mechanical stirrer and electrodes for measuring pH and redox potential (Eh). After that, the required amount of crushed scrap was in reaction vessel uploaded, then the vessel was placed in a Huber GmbH Unistat thermostat and the temperature in the reactor was adjusted to the desired value. Then which the stirrer, measuring instruments were turned on and the pre-calculated amount of concentrated elemental bromine solution (434 g·dm⁻³) was supplied reading recorded original redox - potential, hereinafter in the course of the reaction, adjusting the pH injected 20 g·dm⁻³ NaOH solution if necessary. The gold and copper contents in the solution were analyzed on an ISP-OES instrument. The leach residue was washed, dried, weighed, and the whole sample was decomposed sequentially: first with 6 mol · dm⁻³ with a HNO₃ solution, and then in a solution of aqua regia at 303.5 K, the resulting solutions were analyzed by ISP-OES. Thus, the recovery degree of copper, silver, gold and related platinum group metals was calculated according to the mass balance.

Results and discussion

The Thermodynamics of gold and related metals dissolution in the bromine-bromide system.

The Thermodynamics of the bromine-water system

Bromine is a non-polar hydrophobic compound and its solubility in water is not large, and the following equilibria are observed, as a result of hydrolysis in aqueous solutions (5-7):

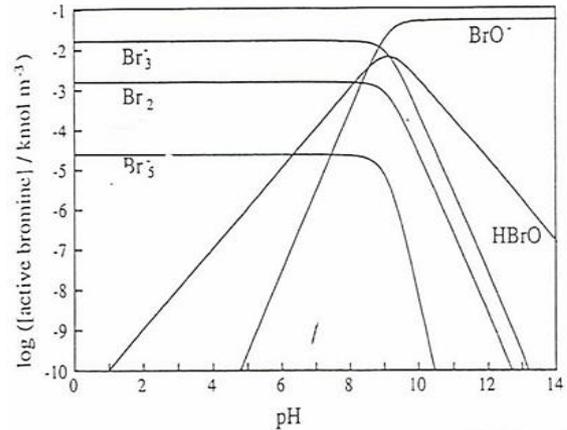
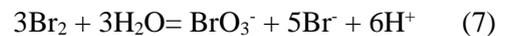


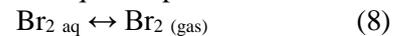
Fig. 1. The $\log a_{\text{Br}_2}$ – pH diagram for the bromine – water system at 298K [9].

Thus, the hydrolysis of bromine proceeds according to the equation:



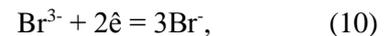
For a stable bromine-water system, Fig. 1 shows that there is a stability region for both bromate (V) and bromate (VII).

At a low bromine content, the bromate (VII) is presented in the form of aqueous particles:



$$\log (\text{Br}_{2 \text{ aq}}) = -0.732 \quad (9)$$

The formation of bromide tri- bromide ions is possible, as an electrochemical process:



but it may also be due to a chemical reaction between bromine and bromide

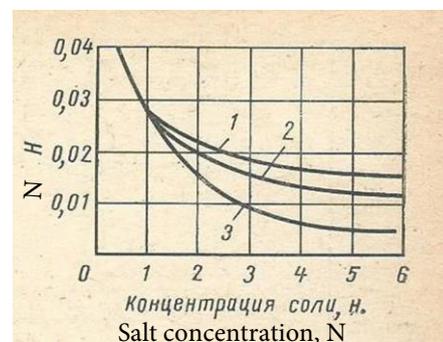
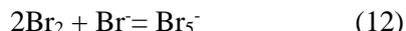


Fig. 2. [10] Dependence of the distribution coefficient of bromine H between the gas phase and bromide solutions on their concentration at 298K: 1- NaBr, 2- FeBr₃, 3- NH₄Br

Tri-bromide ions prevail only for bromide activities exceeding $0.89 \text{ mol} \cdot \text{dm}^{-3} \text{ Br}^-$. Further addition of a bromine molecule leads to the formation of penta-bromide:



Bromate (I) and bromic (I) acids are not shown in Fig. 3 (Eh-pH diagram), since they are thermodynamically less stable than bromate (V) and bromate (VII).

System $\text{Br}_2 - \text{Br}^- - \text{H}_2\text{O}$

The bromine distribution between the gas phase and bromide solutions for KBr, NaBr, FeBr_3 , and NH_4Br was studied [10]. With an increase in the concentration of bromide ion in water, the solubility of bromine in the bromide medium first rapidly increases, the distribution coefficient decreases accordingly, and then this decrease sharply slows down (Fig. 2). Therefore, in a neutral and slightly acidic environment, where hydrolysis proceeds slightly, a solution of bromine in bromide can be used to dissolve gold.

Au- $\text{Br}_2 - \text{Br}^- - \text{H}_2\text{O}$ system

As can be seen from the Eh-pH diagram [9] (Fig. 3) in the presence of bromide ions, gold dissolves in the form of a tetra-bromo-complex, with the exception of a narrow potential range in which the di-bromo-complex is more stable:

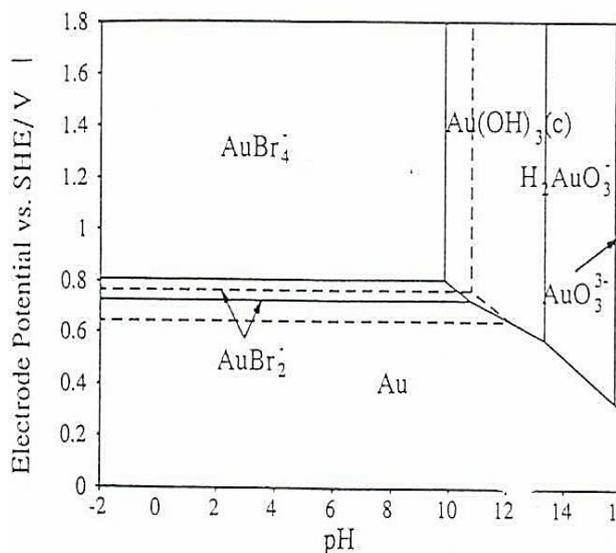
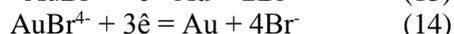
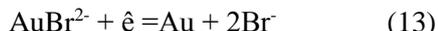


Fig. 3 E-pH diagram for the gold-bromine-bromide system at 298 K and $\alpha_{\text{Au}} = 1$ (—), $\alpha_{\text{Br}} = 5$ (----); the behavior of the bromide ion is taken without regard to its activity coefficient [9]

Moreover, both bromo-complexes are more stable than the chloride alternatives of the same composition and prevail to a pH of about 9, therefore, according to forecasts, the leaching of gold using bromine can work in a wider pH range than with chlorine.

The disproportionation of di-bromoaurate (I) ions proceeds according to reaction (15):



$3\lg(\text{AuBr}_2^-) = -5.25 + \lg(\text{AuBr}_4^-) + 2\lg(\text{Br}^-)$ and has an equilibrium constant of $10^{-5.25}$, which indicates that AuBr_2^- ions are more resistant to disproportionation than their chlorine counterparts.

Dadgar A. et al. [11], Pesic B. and Sargent R. [12,13] showed that the kinetics of gold bromination was significantly faster than when gold cyaniding, due to the higher redox potential of the oxidizing agent [13]. The leaching rates of gold from printed circuit boards were at the level of the best cyanidation rates of the computer scrap samples. The study of kinetics using a rotating disk, which was performed by a printed plateau, showed that the bromination reaction is a chemically controlled process [13] at $\text{pH} < 8$, above which the leaching rate decreases to zero due to limitations of gold solubility. In the preliminary experiments, we showed that the process of bromination at $\text{pH} < 8$, in addition to more favorable kinetics, is distinguished by selectivity, specifically as the copper at bromination process does not go into solution as a result of the formation of a passivating oxide film (Cu_2O) on the surface of copper particles while with cyanide copper forms stable water-soluble anionic complexes.

However, the dissolution of gold in the $\text{Br}_2 - \text{Br}^- - \text{H}_2\text{O}$ system with the formation of anionic gold bromide complexes is accompanied by hydrolysis of the total reaction:



which causes acidification of the medium and a pH shift towards the formation of soluble copper bromide compounds, which is accompanied by a decrease in the concentration of active bromine. We have studied the process of gold dissolution in the bromine-bromide system in the presence of a phosphate buffer solution (NaH_2PO_4) to constantly maintain the pH at a given level. In the table. Figures 2–4 present experimental data on the kinetics of gold leaching from pre-ground (-0.5 – 2 mm) samples of PCB concentrate with varying pH values from 8 to 6.16.

Table 2 Kinetics of gold leaching in bromine - bromide system at pH 8.0

Duration, min	Solution of Br ₂ , ml	[Br ₂], gr·dm ⁻³	Eh, mB	pH	Solution of NaOH, ml	E _{Au} , %	E _{Cu} , %
0	2	1.4	878	7.91	1.5	-	-
10	4	3.1	884	7.89	1.6	-	-
20	6	2.8	882	7.86	1.8	2.4	-
30	8	3.6	883	7.90	1.8	3.5	-
40	10	3.6	881	7.85	1.8	4.5	1.4
60	11	3.4	880	8.06	1.9	4.8	1.2
80	12	3.2	880	7.84	1.9	5.2	1.1
90	13	3.0	890	7.70	1.9	5.9	0.6
110	14	2.8	889	7.91	2.0	4.6	0.6
120	14	2.8	887	7.93	2.1	3.8	0.4
180	14	2.8	887	7.77	2.2	3.6	0.2
Solid loss of gold, %					96.4		

Table 3 Kinetics of gold leaching in bromine - bromide system at pH 7.00

Duration, min	Solution of Br ₂ , ml	[Br ₂], gr·dm ⁻³	Eh, mB	pH	Solution of NaOH, ml	E _{Au} , %	E _{Cu} , %
0	1	1.6	893	7.01	1.2	-	-
10	2	3.5	896	7.01	1.3	12.6	-
20	3	3.6	888	7.04	1.3	22.1	-
30	4	3.9	902	7.05	1.4	34.7	2.3
40	5	4.0	896	7.03	1.5	46.7	2.6
60	6	3.6	897	7.01	1.5	53.8	1.8
80	6	3.6	897	6.98	1.5	55.3	1.8
90	6	3.1	896	6.99	1.5	68.2	1.6
110	6	3.1	896	6.99	1.5	72.4	1.4
120	7	2.9	896	6.99	1.5	77.8	1.2
180	11	2.6	894		1.5	84.4	1.2
Solid loss of gold, %					14.4		

Table 4 Kinetics of gold leaching in bromine - bromide system at pH 6.16

Duration, min	Solution of Br ₂ , ml	[Br ₂], gr·dm ⁻³	Eh, мВ	pH	Solution of NaOH, ml	E _{Au} , %	E _{Cu} , %
0	2	1.8	894	6.16	-	-	-
10	4	4.4	905	6.11	-	16.4	-
20	6	5.2	908	6.12	-	27.4	2.6
30	8	6.1	911	6.14	-	36.2	2.8
40	10	4.9	912	6.12	1	48.2	3.2
60	11	5.2	910	6.20	1	56.7	3.4
80	12	5.8	910	6.16	1	66.4	3.6
90	13	6.1	910	6.12	1	69.8	3.8
110	14	6.6	907	6.09	1	75.9	4.4
120	14	6.4	907	6.06	1	88.7	4.2
180	14	6.1	907	6.12	1	98.9	4.0
Solid loss of gold, %					1.0		

As can be seen from the data presented in table. 2-4, a noticeable leaching of gold in the Br₂-NaBr-NaOH-NaH₂PO₄·H₂O system begins at pH <8 and at pH 6 almost all the gold goes into solution. A sufficient concentration of active bromine in solution for the successful oxidative leaching of gold under these conditions can be considered 6.6 g·dm⁻³ Br₂ at a concentration of bromide of 20 g·dm⁻³ NaBr.

The increased bromine consumption at pH 8.0 and 6.0 observed in the experiments occurs in the first case due to hydrolysis by reactions (5–7) with the formation of very weak oxidizing agents BrO³⁻ (V) and BrO⁴⁻ (VII) bromates [9], and in the second case

the concentration of bromine decreases as a result of the associated oxidation of copper and related metals. It should be noted that by the method of x-ray phase analysis it was found that if at pH 8 copper is oxidized on the surface to a dense film of copper (I) oxide resistant to dissolution, then at pH 6 grains of poorly soluble CuO and CuBr₂ appear along with the bulk of brown cuprite Cu₂O·3Cu(OH)₂.

In Tables 5 and 6 there is the experimental data on the effect of a buffer solution concentration in the range of 30–50 g·dm⁻³ NaH₂PO₄·H₂O on the kinetics of gold and copper leaching at a concentration of 20 g·dm⁻³ NaBr bromide.

Table 5 Kinetics of gold leaching in the bromine - bromide system at an initial pH of 5.5, the volume of a solution of bromine 20 ml and 30 g dm⁻³ NaH₂PO₄·H₂O

Duration, min	[Br ₂], gr·dm ⁻³	Eh, мВ	pH	Solution NaOH, ml	E _{Au} , %	E _{Cu} , %
0	32.60	901	5.50	0.4	-	-
20	30.40	893	5.15	0.8	45.20	2.8
40	25.98	891	4.75	1.6	74.08	3.4
60	23.50	888	4.80	3.6	82.76	3.6
80	23.00	886	5.22	5.5	88.74	4.2
90	22.50	885	5.15	6.2	97.52	4.6

Table 6 Kinetics of gold leaching in a bromine - bromide system at an initial pH of 5.2, a volume of a solution of bromine of 20 ml and a concentration of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ equal to $50 \text{ g} \cdot \text{dm}^{-3}$

Duration, min	$[\text{Br}_2]$, $\text{gr} \cdot \text{dm}^{-3}$	Eh, mB	pH	Solution NaOH, Σ ml	E_{Au} , %	E_{Cu} , %
0	32.80	895	5.27	0.2	-	-
20	33.52	895	5.12	0.4	62.43	2.4
40	28.84	896	5.20	0.8	92.53	2.8
60	25.48	897	5.16	0.8	96.40	3.0
80	24.53	896	5.08	0.8	96.20	3.4
90	22.86	896	5.07	0.8	96.60	3.8

Looking at the experimental data presented in table 5 and 6, we can conclude that an increase in the concentration of the buffer solution significantly reduces the consumption of alkali to maintain a given pH. In addition, it was noted that a higher content of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in the leach solution slightly reduces the transfer of copper to the solution, and an X-ray phase analysis of the leach residue made it possible

to identify CuH_2PO_4 grains in the washed scrap along with Cu_2O , CuO and AgBr . In the next series of experiments, we studied the effect of the concentration of active bromine (Br_2) on the rate and completeness of gold leaching and the behavior of copper at a concentration of $20 \text{ g} \cdot \text{dm}^{-3}$ NaBr bromide. The obtained experimental data is summarized in the tables 7 and 8.

Table 7 Kinetics of gold leaching in the bromine - bromide system at an initial pH of 5.0, a bromine solution volume of 10 ml and $60 \text{ g} \cdot \text{dm}^{-3}$ $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

Duration, min	$[\text{Br}_2]$, $\text{gr} \cdot \text{dm}^{-3}$	Eh, mB	pH	Solution NaOH, ml	E_{Au} , %	E_{Cu} , %
0	14.26	916	5.03	0.1	-	-
20	14.22	908	5.34	1.0	69.43	1.4
40	12.84	892	5.67	4.5	81.23	1.8
60	10.48	891	5.06	4.7	95.43	2.0
90	9.93	889	5.18	5.4	97.20	3.4
120	7.73	860	5.55	10.6	96.74	3.6
160	3.50	860	5.60	12.2	96.10	3.2
180	5.95	860	5.60	20.2	89.26	1.8

Table 8 Kinetics of gold leaching in a bromine - bromide system at an initial pH of 5.2, a volume of a solution of bromine of 20 ml and $60 \text{ g} \cdot \text{dm}^{-3}$ $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

Duration, min	$[\text{Br}_2]$, $\text{gr} \cdot \text{dm}^{-3}$	Eh, mB	pH	Solution NaOH, мл	E_{Au} , %	E_{Cu} , %
0	34.26	895	5.27	0.4	-	-
20	33.64	896	5.12	0.4	62.43	2.6
40	28.84	882	5.20	0.8	92.53	2.8
60	26.48	898	5.16	1.4	96.43	3.0
80	24.66	896	5.08	1.4	96.20	3.4
90	22.74	894	5.07	1.6	97.60	4.6

As can be seen from the data presented in table 7 and 8, a change in the initial concentration of active bromine in the range of 14.26–34.26 g·dm⁻³ Br₂ upon leaching for 0–90 min does not significantly affect the rate and the degree of the gold recovery. With an increase in the duration of leaching, when the bulk of the gold acts as a protective layer, has gone into solution and almost the entire surface of copper contact networks becomes open, the concentration of active bromine drops sharply and the kinetic dependence of the degree of leaching of gold passes through a maximum and begins to decrease. Intensive oxidation of copper is accompanied by acidification of the medium and increased consumption of alkaline solution for pH correction.

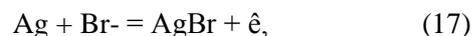
It should be noted that, judging by the results of laboratory experiments, the amount of bromine consumed in the leaching process was 89-95 kg Br₂ per ton of scrap. In order to reduce bromine consumption and find new ways to concentrate gold, the leaching process with the circulation of the productive solution was studied, and the concentration of active bromine was allowed to be adjusted by discrete supply of calculated quantities of a solution of 435 g·dm⁻³ Br₂ and a buffer solution of 60 g·dm⁻³ NaH₂PO₄·H₂O.

The table 9 shows the experimental data of countercurrent leaching of 7 representative samples of a regular PCB concentrate, previously ground to a particle size of 0.5-2 mm, the duration of each stage is 160 minutes. In the first stage, a solution was used after leaching a representative sample of a regular PCB concentrate under standard conditions with an initial concentration of active bromine of 34.26 g·dm⁻³ Br₂. The results are shown in table 9 show that by turning the productive solution over five leaching stages, it is possible to increase the gold concentration by 3.5 times from 44 to 152 ppm. In this case, the degree of transition of gold into solution falls within acceptable limits from 98.23 to 76.58%. We can assume that if leaching is carried out in

countercurrent, then the completeness of extraction and a high degree of gold concentration can be maintained. At the same time, it should be noted that through the use of a reverse leach solution for dissolving gold from five samples of regular PCB scrap, even with correction of the active bromine concentration, it was possible to reduce the oxidizer consumption from 89-95 to 20-32 kg Br₂ per ton of scrap.

Silver, palladium and platinum in the bromine-bromide system

As mentioned earlier, the electronic scrap is a complex raw material of precious metals and, in addition to gold, contains industrially significant concentrations of platinum group metals, especially palladium. In the process of gold leaching in a productive solution, in addition to gold (52 ppm), traces of iron (3.4 ppm) and copper (6-8 ppm) were found. Silver, palladium and platinum in the solution were not detected. Silver was previously detected in the leaching residue in the form of metal inclusions coated on the surface with a dense AgBr film, which is easily formed under conditions of gold leaching by the reaction:



which is thermodynamically expressed by equation (18)

$$\varphi = 0.03 - 0.0591 \lg [\text{Br}^-] \quad (18)$$

Chemical analysis of the solid residue after bromine-bromide leaching of gold from palladium-rich PCB scrap showed the content in it, wt., %: 17.34 Cu, 4.18 Al, 5.16 Sn, 1.83 Fe, 2.26 Zn, 4.18 Pb, 0.520 Ag, 0.00003 Au, 0.036 Pd and 0.0005 Pt. In this sample, the search experiments were carried out (Tables 10-12) to study the conditions for the extraction of silver, palladium and platinum in the bromine-bromide system.

Table 9 The results of gold leaching in the bromine - bromide system at an initial pH of 5.1 with a phase ratio T: W = 3: 1 with a turnover of the productive solution

Stage	[Br ₂] start	[Br ₂] end	Br, ml	NaOH, ml	Buffer solution, ml	Eh, mB	pH	[Au], Ppm start	[Au], Ppm end	E Au, %
I	34.26	22.5	-	1.6	-	894	5.1	44	76	98.23
II	13.72	18.7	1.6	2.3	19.2	911	5.8	68	112	92.56
III	16.8	12.5	2.4	3.4	32.4	897	6.3	100	140	87.30
IV	10.4	11.6	3.2	3.8	58.6	901	5.2	128	164	81.65
V	7.9	10.2	4.0	4.2	68.9	899	5.8	152	195	76.58

Table 10 Kinetics of leaching of silver and palladium in the bromine - bromide system at an initial pH of 6.0, the volume of bromine solution is 14 ml, the phase ratio T: W = 1: 3 and the concentration of bromide ions is 103.5 g·dm⁻³

Duration, min	[Br ₂], gr·dm ⁻³	Solution NaOH, Σ ml	Eh, mB	pH	E _{Ag} , %	E _{Pd} , %
0	23.20	2.0	879	6.0		
60	23.10	2.0	876	5.8	14.15	6.23
240	22.84	2.2	874	5.9	26.72	12.10
300	22.43	2.4	874	5.9	34.15	17.82
360	22.28	2.4	874	5.8	48.92	29.15
900	22.13	2.4	877	5.8	82.35	61.66

Table 11 Kinetics of leaching of silver and palladium in the bromine - bromide system at an initial pH of 1.98, a bromine solution volume of 16 ml, a phase ratio of T: W = 1: 5 and a concentration of bromide ions of 100.5 g·dm⁻³

Duration, min	[Br ₂], gr·dm ⁻³	Solution HBr (62%), Σml	Eh, mB	pH	E _{Ag} , %	E _{Pd} , %
0	29.86	0.2	879	1.98		
60	26.10	0,2	846	1.50	38.62	16.83
240	22.84	0.3	834	1.50	53.25	38.16
300	18.43	0.8	812	1.50	72.62	57.82
360	22.28	2.4	774	1.50	92.37	79.15
900	22.13	2.4	784	1.50	95.62	93.20

The experimental results showed that at pH 6, silver and palladium begin to dissolve only at a high concentration of bromide ions. In this case, 82.35% silver and only 61.66% palladium can be converted into a solution. To transfer all palladium into a solution, the pH must be shifted to the acidic region to pH 1.98-1.5. Silver is quite completely dissolved in a wide range of pH 1.5-6.0. The results obtained are in good agreement with the well-known fact that hardly soluble silver (I) halide in the presence of an excess of halide ions forms soluble highly charged anionic complexes [14, 15]. For AgBr, this can be described by the following reactions:



In the case of palladium, it is known that its oxidation, for example, with nitric acid, in the presence of bromide ions results in the formation of a brown mass of PdBr₂, which is hardly soluble in aqueous medium, but soluble in hydrobromic acid [15]. As can be seen from the experiments, the dissolution of palladium with the formation of the anionic complex of palladium (II) PdBr₄²⁻ can be described, thermodynamically very likely, by reaction (21):



$$\varphi = 0.49 + 0.0296 \log [\text{PdBr}_4^{2-}] - 0.0296 \log P_{\text{Br}_2} - 0.0591 \log [\text{Br}^-]$$

Dependent on the concentration of bromide ions. However, in practice, the process proceeds

slowly, since it is passivated by the formation on the surface of particles of palladium dibromide -PdBr_2 , which is hardly soluble at pH 5-7, and therefore, the dissolution is practically not completed. In the presence of hydrobromic acid (pH 1.98) and an excess of bromide ions, judging by the leaching duration, the process is also accompanied by the formation of a palladium dibromide film, which then dissolves in the acid.

As can be seen from the data given in table. 15 and 16, the dissolution of palladium in the bromine-bromide system proceeds much more slowly in comparison with the behavior of gold. When the medium is acidified with hydrobromic acid and all other things being equal, the recovery of palladium increases from 61.66 to 93.20%. However, if at pH 6.0 only 11 ppm of copper was found in the productive solution, then the acid solution contains, $\text{g}\cdot\text{dm}^{-3}$: 0.0105 Pd, 0.56 Pb, 2.6 Ag, 11.3 Cu. Thus, it was found that at pH 1.98 it was possible to transfer the main amount of palladium and silver into the solution, however, about 20% of the copper passed into the solution. It was not possible to trace the behavior of platinum under the conditions of bromine-bromide leaching of the presented PCB samples, due to its extremely low content.

Thus, it has been experimentally shown that bromine-bromide leaching allows selective and high-speed recovery of gold from electron scrap in an alkaline medium and is an effective alternative to direct cyanidation. The leaching conditions of silver and palladium in the bromine-bromide system are practically presented and theoretically justified. It was shown that during the bromine-bromide leaching in an alkaline medium, the dissolution of copper is impeded by the formation of a passivating film of hardly soluble oxide (Cu_2O) on its surface. However, when silver and palladium are leached, up to 20% of copper is dissolved with a slightly acid bromine-bromide solution, and iron, aluminum, zinc and tin

pass into the solution simultaneously. The dissolution of related metals, especially copper, causes an increased consumption of bromine and complicates the practical use of the technology. Therefore, in further work, the conditions of the joint bromine-bromide leaching of silver, gold, and palladium after preliminary leaching of the accompanying metals and copper from the initial PCB concentrate were investigated.

Findings. A noticeable dissolution of gold in the bromine-bromide system begins at $\text{pH}\leq 8$, and at $\text{pH} = 6$ almost all of the gold passes into the solution quite selectively. A sufficient concentration of active bromine under these conditions can be considered $6.6 \text{ g}\cdot\text{dm}^{-3} \text{ Br}_2$ at a bromide concentration of $20 \text{ g}\cdot\text{dm}^{-3} \text{ NaBr}$.

Leaching with recirculation of the productive solution allowed to reduce the consumption of bromine from 89-95 to 20-32 kg Br_2 per tonne of scrap and to increase the concentration of gold from 76 to 195 $\text{mg}\cdot\text{dm}^{-3}$.

It was shown for the first time that silver and palladium in the studied system ($\text{pH} = 5-6$) can be dissolved only at high concentrations of bromide ions. Complete dissolution of palladium is achieved at a concentration of bromide ions of $100.5 \text{ g}\cdot\text{dm}^{-3}$ and $\text{pH} = 1.5-2.0$.

The high efficiency of bromine-bromide leaching allows further development of the research in the direction of leaching of precious metals in one stage in a slightly acidic medium after preliminary leaching of copper and related metals.

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Бром-бромид жүйесінен алтын, күміс, палладий, платинаны электрондық сынықтардан шаймалау

Коган В. С., Беркович И. В.

Түйіндеме. Электрондық сынықтардан бром- бромид ерітінділерінің, алтын және ілеспе асыл металдардың, мысалы күміс, палладий мен платина сияқты шаймалау термодинамикасы мен кинетикасы зерттелді. Дәстүрлі $\text{Br}_2 - \text{Br}^- - \text{H}_2\text{O}$ жүйесіндегі алтынның көрсететін қасиеттерін теориялық және практикалық талдап, бейтарап және әлсіз қышқылдық ортада бромның гидролизі біршама төмен жүретінін және бромидтегі бром ерітіндісін алтынды шаймалау үшін қолдануға болатындығын дәлелдеді. Сонымен қатар, бром- бромидті шаймалау цианизациямен салыстырғанда анағұрлым қолайлы кинетикасы және селективтілігімен ерекшеленеді. Атап айтқанда, мыс бөлшектерінің бетінде бір валентті мыс оксидінің (Cu_2O) пассивті пленкасының пайда болуы нәтижесінде бейтарап ортада бромдау мыс ерітіндіге өтпейді, ал мыс цианидпен тұрақты еритін анион комплекстерін құрайды. Сілтілік ортадағы рН мәндерін тұрақтандыру үшін фосфатты буферлік ерітінді (NaH_2PO_4) кезіндегі алтынды шаймалау шарттары алғаш рет зерттелді. Активті бром, бромид иондарының концентрациясы және буферлі ерітінді концентрациясының шаймалау ерітіндісіндегі рН мәні, алтынның шаймалау кинетикасына әсері зерттелді. Эксперименталды түрде алтынның айтарлықтай еруі $\text{pH} \leq 8$ -ден басталып, рН 6-да барлық алтын ерітіндіге түсетіні анықталды. Осы жағдайларда белсенді бромның жеткілікті концентрациясын $6,6 \text{ г} \cdot \text{дм}^{-3} \text{ Br}_2$, NaBr бромидтің концентрациясы $20 \text{ г} \cdot \text{дм}^{-3}$ деп санауға болады. Өнімді ерітіндіні циркуляциялау арқылы шаймалау бромды тұтынудың бір тоннасы үшін 89-95-тен 20-32 кг Br_2 азайтуға және алтынның концентрациясын 76-дан $195 \text{ мг} \cdot \text{дм}^{-3}$ -ке дейін арттыруға мүмкіндік берді. Жұмыста алғаш рет, қарастырылып отырған күміс пен палладий жүйесіндегі ($\text{pH}=5-6$) бромид иондарының жоғары концентрациясында ғана айтарлықтай ери бастайтыны зерттелген. Палладийдің толық еруі $100 \text{ г} \cdot \text{дм}^{-3}$ ион бромидінде және $\text{pH} = 1,98$ деңгейінде болды.

Түйін сөздер: алтын гидрометаллургиясы, компьютерлік сынықтар, броммен асыл металдардың еруі термодинамикасы мен кинетикасы, фосфатты буферлік ерітінді.

Выщелачивание золота, серебра, палладия и платины из электронного скрапа в бром-бромидной системе

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Аннотация. Изучена термодинамика и кинетика выщелачивания золота и сопутствующих благородных металлов, таких как серебро, палладий и платина, из электронного скрапа бром-бромидными растворами. Теоретический и практический анализ поведения золота в традиционной системе $\text{Br}_2 - \text{Br}^- - \text{H}_2\text{O}$ подтвердил факт, что в нейтральной и слабощелочной среде, когда гидролиз брома протекает незначительно, раствор брома в бромиде можно использовать для выщелачивания золота. При этом бром-бромидное выщелачивание по сравнению с цианированием отличается более выгодной кинетикой и избирательностью. В частности, медь при бромировании в нейтральной среде в результате формирования на поверхности частичек меди пассивирующей пленки оксида одновалентной меди (Cu_2O), не переходит в раствор, в то время, как с цианидом медь образует устойчивые растворимые анионные комплексы. С целью стабилизации значений рН в щелочной области впервые исследованы условия выщелачивания золота в присутствии фосфатного буферного раствора (NaH_2PO_4). Изучено влияние на кинетику выщелачивания золота рН выщелачивающего раствора, концентрации активного брома, бромид-ионов и концентрации буферного раствора. Экспериментально установлено, что заметное растворение золота начинается при $\text{pH} \leq 8$, а при рН 6 в раствор переходит практически все золото. Достаточной концентрацией активного брома в этих условиях можно считать $6,6 \text{ г} \cdot \text{дм}^{-3} \text{ Br}_2$ при концентрации бромид-ионов $20 \text{ г} \cdot \text{дм}^{-3} \text{ NaBr}$. Выщелачивание с рециркуляцией продуктивного раствора позволило снизить расход брома с 89-95 до 20-2 кг Br_2 на тонну скрапа и поднять концентрацию золота с 76 до $195 \text{ мг} \cdot \text{дм}^{-3}$. В работе впервые показано, что серебро и палладий в изучаемой системе ($\text{pH}=5-6$) начинают заметно растворяться только при высоких концентрациях бромид-ионов. Полное растворение палладия было достигнуто при $100 \text{ г} \cdot \text{дм}^{-3}$ бромид-ионов и значениях $\text{pH}=1,98$.

Ключевые слова: гидрометаллургия золота, компьютерный скрап, термодинамика и кинетика растворения благородных металлов бромом, фосфатный буферный раствор.

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Исследование влияния пластификаторов и термопластов на механические свойства эпоксидной смолы и углепластика (Обзор)

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Аннотация. Задача создания технологии упрочнения эпоксидной смолы (ЭС) и углепластика актуальна для многих разделов техники: космической, авиационной, оборонной, автомобильной и др. Вопрос решается многочисленными приемами модификации ЭС, компонентов углепластика. Модификация ЭС осуществляется путем ввода различных химических соединений. Одним из методов упрочнения углепластика является модификация пластификаторами (трикрезилфосфат, олеиновая кислота) или термопластами (полисульфон, поликарбонат, полистирол, ударопрочный полистирол). В работе собраны имеющиеся в литературе экспериментальные данные по влиянию различных видов модификаторов на прочность ЭС и углепластика. Проанализирован механизм модифицирования ЭС и углепластика пластификаторами и термопластами. Введение пластификаторов в качестве модификаторов ЭС приводит к улучшению ударной вязкости в 2 раза. Оптимальный ввод пластификаторов в ЭС составляет 15 % и зависит от полноты растворимости в связующем, дальнейшее увеличение ввода пластификатора приводит к снижению прочности материала. Модификация термопластами углепластика может привести к улучшению прочности на сжатие на 20% и ударной вязкости в 2 раза. При введении термопластов свыше 20% в углепластик показатели прочности снижаются. Полученные данные необходимы для разработки отечественной технологии производства ударопрочных углепластиков.

Ключевые слова: эпоксидная смола, модификаторы, пластификаторы, термопласты, термообработка, ударная вязкость, прочность.

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Введение

Углепластик – это композитный материал (КМ), созданный на основе эпоксидной смолы (ЭС), играющий роль матрицы и углеродного

волокна, выполняющий функции арматуры [1, 2, 26, 27]. Армированные пластики обладают рядом преимуществ по сравнению с такими более распространенными конструкционными материалами, как алюминий, титан, сталь и

другие сплавы, благодаря малому весу, высоким удельным упруго-прочностным характеристикам, химической стойкости, однако, существуют недостатки. Наиболее существенным является – низкая сопротивляемость ударному воздействию ЭС и углепластика.

В настоящее время в развитии углепластиков актуальна задача поиска путей повышения ударной вязкости при сохранении достигнутых уровней статической прочности. Увеличение ударной вязкости углепластика осуществляется приемами модификации путем введения специальных добавок: термопласты, пластификаторы [3-6]. Экспериментальным исследованиям по проверке возможностей этого метода, должен предшествовать подробный литературный анализ имеющихся публикаций.

Цель настоящей работы – анализ литературных данных по модификации и упрочнения ЭС и углепластика путем введения различных видов модификаторов.

1 Виды модификаторов эпоксидных смол, в том числе пластификаторы и термопласты

Одним из методов модификации углепластика является *пластификация* – изменение свойств полимера путем добавления в композицию низкомолекулярную добавку – пластификаторов. Пластификаторы изменяют вязкость системы, гибкость и подвижность молекулярных структур. Многие пластификаторы позволяют повысить ударную вязкость полимера без потери прочности и модуля упругости, также могут улучшить огневую, световую и тепловую устойчивость. Среди пластификаторов интерес представляют трикрезилфосфат (ТКФ) и олеиновая кислота (ОК) за счет их совместимости с ЭС [7,8].

Трикрезилфосфат – это сложный эфир ортофосфорной кислоты трикрезола или дикрезола (рисунок 1).

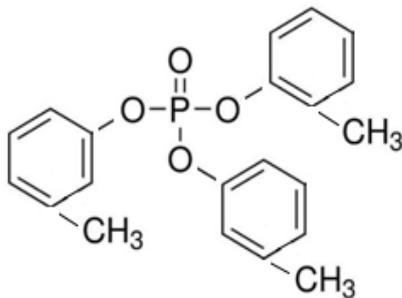


Рисунок 1. Химический состав трикрезилфосфата

ТКФ легко растворяется в жирах, маслах и во многих органических растворителях, не растворим в воде. ТКФ стабилен при нормальных температурах и давления, а его точка кипения лежит в пределах 280-290 °С, что исключает образования паров во время работы. ТКФ часто применяется в космической, реактивной технике и авиации.

Олеиновая кислота – мононенасыщенная жирная кислота, содержащую в молекуле только одну ненасыщенную связь, относится к группе Омега-9 ненасыщенным жирным кислотам (рисунок 2). По физическим свойствам ОК представляет собой бесцветную вязкую жидкость с температурой плавления от 13,4 до 16,3 °С, температурой кипения 286 °С и плотностью 0,895 г/см³. ОК растворяется в органических растворителях и не растворяется в воде. ОК распространён в виде ненасыщенных жирных кислот и содержится в растительных и животных жирах. ОК применяют в качестве компонентов моющих средств, лаков, олиф, эмульгаторов и пластификаторов.

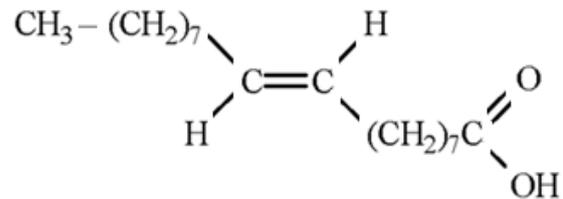


Рисунок 2. Химический состав олеиновой кислоты

К этому классу термопластов относят полимеры:

1 Полистирол

Полистирольные пластики (ПС) представляют собой многочисленную группу термопластичных материалов, химический состав полимерной части которых содержит мономер стирол или продукты его сополимеризации.

Процесс образования полимера полистирола из мономера стирола изображено на рисунке 3 следующим образом:

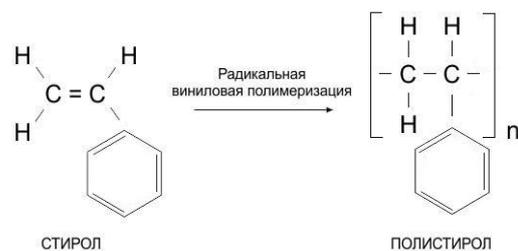


Рисунок 3. Химический состав полистирола

Вследствие прозрачности ПС относят к группе органических стекол. Плотность полистирола выше плотности воды и составляет 1050–1100 кг/м³. Температура плавления полистирола 190-230^oC [5].

2 Ударопрочный полистирол

Ударопрочный полистирол (УПС) обладают более высокой термостойкостью и стойкостью к ударным нагрузкам. УПС температура плавления 190-230^oC. Образование ударопрочного полистирола показано на рисунке 4 [5].

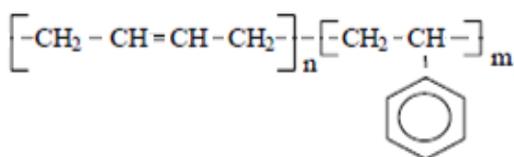


Рисунок 4. Химический состав ударопрочного полистирола

3 Поликарбонат

Поликарбонат (ПК) – сложные полиэфиры угольной кислоты и двухатомных спиртов, химический состав которого приведен на рисунке 5. Наибольшее промышленное значение имеют ароматические поликарбонаты, в первую очередь, поликарбонат на основе Бисфенола А, синтезируемого конденсацией фенола и ацетона. ПК температура плавления 220-240 ^oC[5].

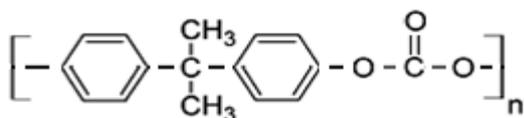


Рисунок 5. Химический состав поликарбоната

4 Полисульфон

Полисульфоны (ПСФ) – полимеры, содержащие в основной цепи повторяющиеся группы SO₂, химический состав, которого изображен на рисунке 6. ПСФ – аморфные прозрачные термопластичные полимеры от светло-желтого до коричневого цвета, молекулярной массой (30-60)10³. ПСФ температура плавления 245-400^oC [5].

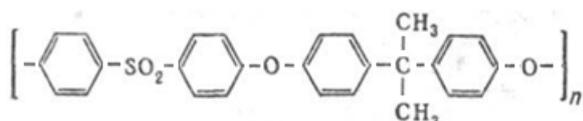


Рисунок 6. Химический состав полисульфона

2 Исследование влияния пластификаторов и термопластов на прочность ЭС и углепластика

Влияние пластификаторов. Авторами в работе [9] были изучены влияние ТКФ на свойства эпоксидного композита на основе ЭД-20 с применением двух типов отвердителя: полиэтиленполиамин (ПЭПА) и низкомолекулярный полиамид марки ПО-300. В результате проведенных исследований было установлено, что содержание пластификатора ТКФ в количестве 30 масс.ч. для составов отверженных ПЭПА, достигаются более высокие показатели разрушающего напряжения при изгибе в 2 раза, ударной вязкости в 4 раза, как показано в таблице 1.

Таблица 1. Свойства эпоксидных композитов

Состав композиции, 15 масс.ч. ПЭПА	Разрушающее напряжение при изгибе, МПа	Ударная вязкость, кДж/м ²	Твердость по Бринеллю, МПа
100ЭД-20	17	3	225
70ЭД-20+30ТКФ	34	13	84

При введении в ЭС пластификатора ТКФ, отверженный ПО-300, устойчивость к удару увеличивается в 2,5 раза, значение которого составляет 36 кДж/м², в случае испытания на изгиб не происходит разрушения образца (таблица 2).

Таблица 2. Свойства эпоксидных композитов

Состав композиции, 40 масс.ч. ПО-300	Разрушающее напряжение при изгибе, МПа	Ударная вязкость, кДж/м ²	Твердость по Бринеллю, МПа
100ЭД-20	76	13	185
70ЭД-20 +30ТКФ	8*	36	-

Примечание: * - не разрушается

Авторами в работе [10] были исследованы свойства эпоксидных композиций на основе эпоксидной диановой смолы марки ЭД-20 и отвердителем ПЭПА с добавлением оболочки гречихи и проса, трихлорэтилфосфата и ТКФ. ТКФ применяли в качестве пластификатора и замедлителя горения. При использовании состава 70 ЭД-20 + 30 ТКФ + 15ПЭПА были получены наиболее оптимальные комплексные свойства. Физико-механические и теплофизические свойства этого состава

выглядят следующим образом: ударная вязкость повысилась от 9 до 14 кДж/м² по сравнению с составом без модификатора ТКФ, разрушающее напряжение при изгибе увеличилось в два раза, что составляет 98 МПа.

В работе [11] разработаны составы на основе смолы ЭД-20 с модификаторами ТКФ. В качестве отвердителя смолы использовали отвердитель ПЭПА. Образцы получали в виде прессованных таблеток с толщиной 1 мм с содержанием 70% от массы ЭД-20, 15% ПЭПА, 30% ТКФ. Испытания проводили на изгиб, ударную вязкость и определяли такие показатели, как время гелеобразования, время и температура отверждения эпоксидных композиций. Результаты исследования показали, что введение в состав смолы пластификатора ТКФ улучшает ударную вязкость в 3 раза (10 кДж/м²), изгиб в 3 раза (57 МПа), твердость на 59% (197 МПа). Также увеличивается время гелеобразования от 24 до 60 мин., время отверждения от 39 до 115 мин и снижает температуру отверждения от 125 до 44 °С.

В работе [12] изучали влияния добавок на физические свойства смолы. В качестве смолы использовали ненасыщенную полиэфирную смолу с введением триэтилфосфата, ТКФ. После смешивания и обработки ультразвуком образцы отверждали в печи 3 часа при 70 °С, 1 час при 100 °С и 1 час при 150 °С. Образцы испытывали и определяли предел прочности на изгиб, модуль упругости. Предел прочности на изгиб увеличился от 88 до 94 МПа, модуль упругости 0,63-0,7*10⁶ кгс/см².

Авторами [13] были исследованы влияние модификаторов на механические свойства смолы. Для получения композита использовали следующие материалы и компоненты: ненасыщенная полиэфирная смола, отвердители – пероксид метилэтилкетон и нафтанат кобальта, модификатор – ТКФ. Концентрация ТКФ в композиции 5%, 10% и 15% от массы смолы. Анализ механических свойств показывает, что введение 5% ТКФ повышает предел прочности на разрыв в 1,3 раза (98 МПа). Добавление 15% ТКФ улучшает ударную вязкость на 12% (1,47 кДж/м²).

В работе автора [14] разработаны и исследованы эпоксидные композиты на основе смолы ЭД-20 с применением пластификаторов. Для отверждения смолы применяли отвердитель аминного типа – ПЭПА. Для пластификации использовали олеиновую кислоту. Концентрация ОК в составе смолы составляет 10%, 15% и 20% от массы смолы. Результаты анализа свойств показывает, что введение ОК повышает устойчивость к изгибам в 6 раз (105 МПа), ударную вязкость в 5.5 раз (17 кДж/м²).

Авторами в работе [15] были исследованы влияния пластификатора диглицидиловый эфир диэтиленгликоля (ДЭГ-1) на механические свойства смолы ЭД-20 с отвердителями ПЭПА и ПО-300. Анализ свойств после испытания показывает, что для образцов, отверженных как ПЭПА, так и ПО-300, наблюдается увеличение ударной вязкости. При содержании 70 масс.ч. ЭД-20, 15 масс.ч. ПЭПА и 30 масс.ч. ДЭГ-1 устойчивость к ударным нагрузкам составил 15 кДж/м², что на 5 раза выше по сравнению со смолой без добавления модификатора.

В случае с ПО-300, при соотношении 60 масс.ч. ЭД-20, 40 масс.ч. ПО-300 и 40 масс.ч. ДЭГ-1 ударная вязкость повысилась от 13 до 20 кДж/м², образцы при изгибе не разрушаются.

Работ, посвященных модификации углепластика пластификаторами отсутствуют. Рассмотрим ряд работ по влиянию термопластов на механические свойства углепластика.

Влияние термопластов. В работе [16] в качестве термопласта использовался поликарбонат марки Lexan. Поликарбонаты — группа термопластов, сложные полиэфиры угольной кислоты и двухатомных спиртов общей формулы (-O-R-O-CO-)n.



Рисунок 7. Зависимость ударной вязкости композиционного материала от концентрации ПК [15]

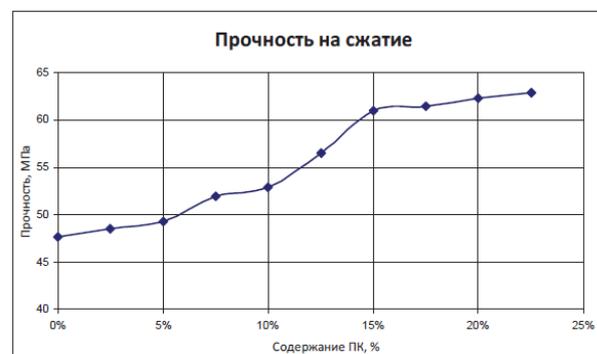


Рисунок 8. Зависимость прочности при сжатии композиционного материала от концентрации ПК [15]

Как видно из рисунков 7 и 8, добавление 15-20% поликарбоната увеличивает ударную вязкость композитного материала почти в 2 раза, кроме того прочность при сжатии увеличилась в 1,5 раза [15].

В работах [17, 18] авторами изучено влияние термопластов полисульфона и полиэфирсульфона на свойства эпоксидной смолы ЭД-20. Показано, что с увеличением содержания полисульфона в ЭС до 20 % ударная вязкость композита увеличивается с начальной величины 24,9 Дж/м² (определялась на приборе типа Дистант) до 103 Дж/м², а прочность на изгиб с 48,8 МПа до 79,9 МПа. В случае модифицирования полиэфирсульфоном, ударная вязкость ЭС достигла максимума 102,3 Дж/м² при 20% содержании модификатора; максимум прочности на изгиб 94,0 МПа достигнут при 5% содержании модификатора, с дальнейшим ростом содержания модификатора прочность монотонно снижается до 75,7 МПа.

В данной работе [19] исследовалось влияние термопластичных модификаторов на термомеханические характеристики отверждённых эпоксидных материалов. Основой для исследуемых систем служила эпоксидная смола ЭД-20, в качестве отвердителя использовали диаминдифенилсульфон (ДАДФС). Модифи-

каторами служили термопластичные полимеры полисульфон (ПСФ), полиэфирсульфон (ПЭСФ), а также их смеси.

В таблице 3 представлены результаты экспериментов на ударную вязкость и сжатие отверждённых образцов с модификаторами.

В [21] рассмотрены слоистые композиты, полученные на основе разных эпоксиполисульфоновых композиций. Прочность при изгибе и межслоевом сдвиге таких углепластиков монотонно возрастает. При этом, для смесей, содержащих 10 масс.% полисульфона прочность возрастает на 35%, 20 масс.% – на 5-20%. Однако, в работе нет данных по вязкости разрушения композитов.

В [22] проводилось исследование углепластиков, полученных на основе эпоксидной матрицы и термопласта полиэфиримида. Установлено, что при увеличении концентрации модификатора, прочность композиционного материала при изгибе возрастает примерно с 68 МПа до 82 МПа (на 20%). Прочность при сдвиге же не зависит от содержания модификатора.

Авторы работы [23] рассматривали углепластики, полученные на основе эпоксидного олигомера и термопластов: полиэфиримида, поликарбоната и феноксида. Все модификаторы в виде порошка вносили между слоями армирующего наполнителя.

Таблица 3. Влияние модификаторов на прочность и ударную вязкость ЭС

Количество Модификатора	T _g , определённая по тангенсу угла механических потерь, °С	T _g , определённая по термодинамической кривой, °С	A, Дж/м ²	σ _{сж} , МПа
Без модификатора	160	165	24,9	48,8
ПСФ 5 %	170	173	67,4	73,2
ПСФ 10 %	178	182	77,0	71,5
ПСФ 20 %	183	187	103,0	79,9
ПЭСФ 5 %	170	172	69,3	94,0
ПЭСФ 10 %	175	179	98,5	88,7
5 %				
ПЭСФ 20 %	184	188	102,3	75,7
ПСФ 2,5 % ПЭСФ 7,5 %	184	188	57,7	66,2
ПСФ 5 % ПЭСФ 5 %	186	190	57,1	79,8
ПСФ 7,5 % ПЭСФ 2,5 %	176	180	49,4	113,0

Прочность углепластика, модифицированный полиэфир-мидом или феноксидом возросла больше чем в 2,5 раза.

В работе [24] при довольно большом содержании модификатора термопласта (40 масс.%), вязкость разрушения композита возросла приблизительно в 2 раза.

3. Механизм модифицирования ЭС и углепластика пластификаторами и термопластами

По литературным данным [14] способов модификации можно разделить на три основные группы: химические, химико-физические и физические, которые, в свою очередь, подразделяются на:

– химические: изменение химического состава смолы, регулирование типа отвердителя и добавление реакция способных добавок;

– химико-физические: легирование, добавление ПАВ, совмещение с инертными пластификаторами и разбавителями, растворимыми в смоле, модифицирование твердых нерастворимых крупнодисперсных добавок (минеральных или органических);

– физические: предварительная ультразвуковая обработка смолы, вибрацией, токами высокой частоты, обработка в процессе отверждения.

Чтобы пластификатор был эффективным, он должен быть тщательно перемешан и включен в матрицу полимера. Обычно это достигается за счет нагрева и смешивания до тех пор, пока либо полимер не растворится в пластификаторе, либо пластификатор не растворится в полимере.

Как правило, термопласт растворяется в эпоксидном олигомере, а в процессе отверждения происходит фазовое разделение, которое инициируется ростом молекулярной массы эпоксидного олигомера [18, 19]. Этот эффект подтверждается в литературе [24], где падение прочности углепластика связано с увеличением термопласта (полисульфон) при повышении его молекулярной массы, в связи с чем термопластичному связующему становится труднее пропитать волокна.

Температурный режим отверждения определяет тип фазового разделения, а, следовательно, размер частиц дисперсной фазы. Тип фазового разделения оказывает существенное влияние на ударную прочность ПКМ. Считается, что выделяющаяся в процессе отверждения фаза полимера образует гомогенную дисперсию с размером частиц менее 1 мкм, обеспечивая снижение внутренних напряжений и повышение ударной вязкости, эластичности и трещиностойкости.

Для достижения наибольшего модифицирующего эффекта добавки необходимо сильное адгезионное взаимодействие между матрицей и включениями. Очевидно, что наиболее прочным межфазное взаимодействие будет при образовании химических связей между фазами, т.е. модификатор должен иметь в своем составе функциональные группы, способные реагировать с одним из компонентов отверждающейся системы [6].

Выводы

Исходя из представленного литературного анализа можно заключить следующее:

1) Упрочнение углепластика перечисленными видами модификаторами в основном получены на широко используемой ЭС «холодного отверждения» ЭД-20, которая отверждается при комнатной температуре 24°C. Недостатком применения такой смолы при изготовлении углепластика является низкая прочность, высокая вязкость и короткое время жизнеспособности. Между тем, в технологии производства углепластика большой интерес представляют ЭС «горячего» отверждения. Одним из представителей ЭС этого класса является ЭС марки – Этал-Инжект-Т, которая отверждается при температурах 150-180°C. При этих температурах ЭС, благодаря низкой вязкости, длительной жизнеспособности обеспечивается хорошее качество пропитки углеволокон и способствует получению углепластика с высокими прочностными характеристиками.

2) введение пластификаторов в качестве модификаторов ЭС приводит к улучшению ударной вязкости в 2 раза;

3) наилучшие показатели прочностных характеристик показывают смолы с 15% введенных пластификаторов;

4) введение термопластов может привести к улучшению прочности на сжатие на 20% и ударной вязкости в 2 раза.

5) при введении термопластов свыше 20% показатели прочности снижаются.

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Пластификаторлар мен термопластикалардың эпоксидті және көміртекті талшықтардың механикалық қасиеттеріне әсерін зерттеу (Шолу)

Мустафа Л.М., Исмаилов М.Б., Ермаханова А.М., Санин А.Ф.

Түйіндеме. Эпоксид шайырын (ЭШ) және көмірпластикті беріктендіру технологиясын жасау мәселесі көптеген техника салалары үшін өзекті болып табылады: ғарыш саласы, авиация, қорғаныс, автомобиль жасау және т.б. Бұл мәселе көмірпластиктің компоненттерін, ЭШ модификациялаудың көптеген тәсілдерімен шешіледі. ЭШ модификациялау түрлі химиялық қоспаларды енгізу жолымен іске асырылады. Көмірпластикті беріктендірудің бір әдісі пластификаторлармен (трикрезилфосфат, олеин қышқылы) немесе термопласттармен (полисульфон, поликарбонат, полистирол, соққыға төзімді полистирол) модификациялау болып табылады. Бұл жұмыста әр түрлі модификаторлардың ЭШ және көмірпластиктің беріктігіне әсері бойынша әдебиетте кездесетін тәжірибелік мәліметтері жинақталған. ЭШ және көмірпластикті пластификаторлармен және термопласттармен модификациялау механизмі талданған. ЭШ модификатор ретінде пластификаторларды енгізу соққы тұтқырлығының 2 есеге жақсаруына алып келеді. ЭШ пластификаторларды енгізудің оптимальді мөлшері 15% және ол байланыстырғыштағы толығымен ерігіштікке тәуелді, пластификатордың енгізу мөлшерінің ары қарай артуы материал беріктігінің төмендеуіне алып келеді. Көмірпластикті термопласттармен модификациялау сығу беріктігін 20% және соққы тұтқырлығын 2 есе арттыруға алып келуі мүмкін. Термопласттарды 20% артық мөлшерде көмірпластикке қосу кезінде беріктік көрсеткіштері төмендейді. Алынған мәліметтер соққыға берік көмірпластиктерді өндірудің отандық технологиясын әзірлеу үшін қажет болып табылады.

Түйін сөздер: эпоксидті шайыр, модификаторлар, пластификаторлар, термопласттар, термиялық өңдеу, соққы тұтқырлығы, беріктігі.

Study of the effect of plasticizers and thermoplastics on the mechanical properties of epoxy and carbon fiber reinforced plastic (Review)

Mustafa L.M., Yermakhanova A.M., Ismailov M.B., Sanin A.F.

Abstract. Increasing strength of epoxide resin (ER) and carbon fiber reinforced plastic (CFRP) is an aim up-to-date for many machinery sections: space, aviation, defense, automotive, and others. The aim is achieved via numerous methods of ER and carbon fiber reinforced plastic modifications. ER modifications is carried through injection of various chemical compounds. One of efficient modifications assumes introduction of plasticizers (tricresyl phosphate, oleic acid) or thermoplastics (polysulfone, polycarbonate, polystyrene, high impact polystyrene). The article contains experimental data of various types of modifiers influence on strength of ER and CFRP available in literature. The mechanism of modifying ER and CFRP with plasticizers and thermoplastics were analyzed. The introduction of plasticizers as ER modifiers leads to a twofold improvement in impact strength. The optimal input of plasticizers in ER is 15% and depends on the completeness of solubility in the binder, a further increase in the input of plasticizer leads to a decrease in the strength of the material. Modification of thermoplastics with CFRP can lead to an improvement in compression strength by 20% and impact strength by 2 times. With the introduction of thermoplastics over 20% in CFRP, strength indicators are reduced. The acquired data is necessary to elaborate domestic technology for production of high-impact CFRP.

Keywords: epoxy resin, modifiers, plasticizers, thermoplastics, heat treatment, impact strength, strength.

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Iron sulphates production being polarized by the direct and alternating currents

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Abstract. The process of iron oxidation in the sulfate electrolytes was studied by the method of electrochemical polarization by the steady and transient currents. Initially, in the first electrolyzer, the iron electrodes were oxidized under the influence of alternating current. The results of iron oxidation in the first electrolyzer were monitored by determining the weight loss of the iron electrodes. An almost rectilinear increase in the mass of iron is established to be observed, which passed into the solution in the form of Fe^{2+} ions when the current density changes in the range of 80-400 A / m^2 . The current efficiency is close to 100%, and sometimes exceeds 100%, since the chemical dissolution of iron in sulfuric acid also occurs simultaneously. The iron sulfate (II) can be obtained by evaporation of the solution. After that, the sulfate solution containing iron ions (II) was sent to the second electrolyzer, in which the oxidation of iron (II) to iron (III) was carried out under the direct current. The electrode spaces were separated by an MA-40 anion exchange membrane. Over 90% of iron (II) was demonstrated to be transfers into the trivalent state within 1 hour in the second electrolyzer at a current density of 120 A / m^2 . A change in the current density to 600 A / m^2 leads to an increase in the oxidation state to 97.5%, i.e. iron ions (II) are almost completely oxidized under the specified conditions. As a result of the experiments, an electrochemical method for producing iron sulfate (III) was developed.

Keywords: iron, electrolyte, sulfate, electrolysis, alternating current.

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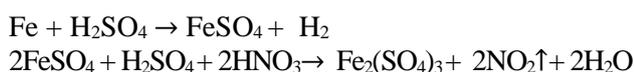
Introduction

Iron forms many compounds being an active element. Its compounds are widely used in various branches of technology and industry. Specifically, there is a research devoted to the development of a

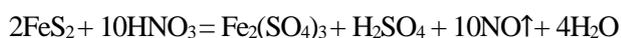
method for producing sulfate and iron oxide nanoparticles: when silica gel and aluminum oxide are impregnated with Fe (II) sulfate solutions, ferric hydroxide and oxysulfate nano-particles are formed on the surface of silica gel, and iron oxide nanoparticles on the surface of aluminum oxide [1, 17,

18]. To say more, iron compounds, namely sulfates, are used in water purification as a coagulant [2-4]. In medicine, various compounds containing both ferrous and ferric iron are also used [5,6]. Iron sulfate (III) can be used as a mordant for dyeing wool and as a background for the enrichment of sour coal. Acidic solutions are used as an oxidizing medium in the extraction of useful components out of ores [7]. Iron ions (III), being active oxidizing agents, are widely used in the technology of subsurface leaching of uranium, although the authors of [8] note that the use of sulfate solutions of ferric iron is associated with the problem of its regeneration. Nevertheless, the researchers [9] used a solution of ferric iron along with the ammonium sulphate and sodium peroxoborate in the study of the comparative sulfuric acid catalytic oxidation of uranium (IV) to uranium (VI).

An existing and frequently used method for producing ferric sulfate is that, first, metallic iron is chemically dissolved in sulfuric acid when heated to produce ferrous ions [10]. Further, the iron ions (II) are oxidized in the presence of nitric acid, while the following reactions proceed:



Grinding of iron to a state of sawdust is noted to be required for a more efficient process, in addition, nitrogen dioxide, a substance that is uncommon for the environment is released as a result of the reaction. This is result in the method has certain disadvantages. Iron sulfate (III) is also obtained by dissolving iron oxide (III) in 75-80% sulfuric acid. In addition, iron sulfate (III) solutions can be obtained by oxidation of pyrites with nitric acid:



There is also a method for producing iron sulfate (III), which serves as a coagulant, by treating pyrite cinder with hot sulfuric acid. The sifted cinder must first be treated with concentrated nitric acid (in the amount of 8-10 kg per 1 g of coagulant). The oxidized cinder is mixed and kept before cooking the coagulant for 5-6 hours. All these methods are described in the monograph of Pozin M.Y. [7].

In order to increase the degree of conversion of ferrous iron to ferric, the authors of [11] propose adding a catalyst in the form of iron tetrasulfophthalocyanine to the solution. The essence of the method lies in the fact that the catalyst is added to the sulfuric acid solution of iron sulfate (II) on carbon fabric and the mixture is stirred in a stream of oxygen. The degree of conversion reaches 83%. Using an anode made of graphite or platinum, it is

proposed to oxidize iron sulfate (II) electrochemically at a temperature of 80°C [12]. The current yield of iron oxidation (II) to iron (III) reaches 95.8%. Considering that, iron sulfates are most widely used in various branches of technology and industry, as well as in medicine, but the existing methods of their producing are imperfect and complex, we believe that the development of new methods for producing iron compounds is an urgent problem. In this regard, the aim of our study is to develop a two-stage method for producing iron sulfate (III) by polarizing iron electrodes, first with alternating current of industrial frequency and then anodic oxidation of the resulting solution on a lead electrode.

Testing method

A set was assembled to conduct electrolysis with alternating and direct current, the circuit diagram of which is provided in Figure 1.

The set consists of 1 and 2 electrolyzers (conventionally named "the first" and "the second" electrolyzers). The first electrolyzer and the cathode space of the second electrolyzer are filled with sulfate electrolyte (4). Iron (3) was used as electrodes in the first electrolyzer, a lead electrode (5) was used as the anode, and titanium (6) was used as the cathode. In the second electrolyzer, interelectrode spaces are separated by an MA-40 anion exchange membrane (7). We used LATR (8) to obtain alternating current, and as a constant current source - Matrix MPS - 3003D (9). An alternating current ammeter E 538 (10) and a direct current ammeter (11) were used to measure the current strength.

A titanium plate cut from titanium sheets of the VT-1-0 brand was used as the electrodes in the experiments, iron of St. 3 brand and lead of C-1. Before electrolysis, the electrodes were cleaned with emery, thoroughly washed with distilled water, wiped with filter paper, and degreased with ethyl alcohol. A sulfuric acid of "chemically pure" was used for an electrolyte solution to be prepared. In the first electrolyzer, the concentration of sulfuric acid was equal to 250 g / dm³. Iron electrodes were polarized by industrial alternating current with a frequency of 50 Hz at various current densities. After dissolution of the iron electrodes by alternating current, the electrolyte from the first electrolyzer was fed into the anode space of the second electrolyzer, in which ferrous iron is oxidized to a trivalent state during anodic polarization. At the end of the experiment, the resulting solution was evaporated, the precipitated crystals were dried and identified by chemical, X-ray phase and X-ray fluorescence methods.

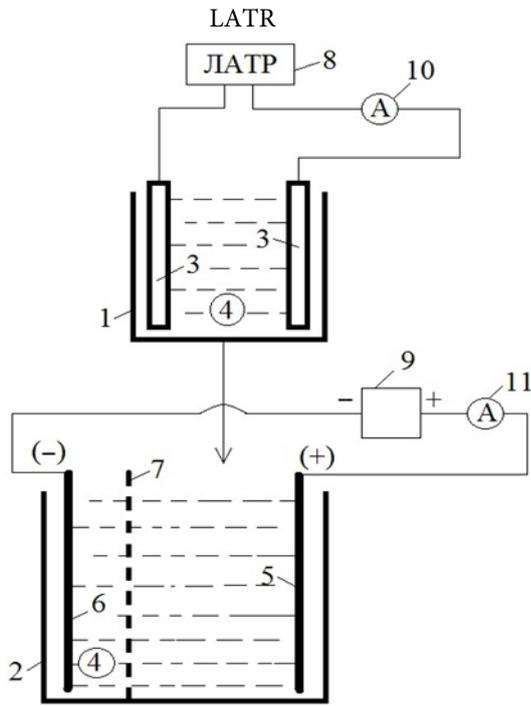
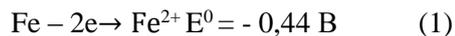


Figure 1 A set flow sheet for producing iron sulfate (III) by two-stage electrolysis: 1 and 2 - the first and the second electrolyzers; 3 - iron electrodes; 4 - sulfate electrolyte; 5 - lead electrode; 6 - titanium electrode; 7 - MA-40 anion exchange membrane; 8 - an alternating current source - LATR; 9 - DC source - current rectifier; 10 - alternating current ammeter; 11 - DC ammeter.

Results and discussion

When the electrodes are polarized in a sulfuric acid solution by alternating current in the first electrolyzer (1), the iron oxidation reaction takes place:

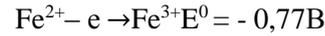


This reaction proceeds in the anode half-cycle of the alternating current.

As the previous studies have established [13, 14], being polarized by alternating current, a targeted course of electrode processes is possible despite the fact that the current direction changes with a frequency of 50 Hz, i.e. within a second, each electrode 50 times becomes either the anode or the cathode. But unlike those processes that occur during polarization by direct current, in this case, the iron manages to oxidize in the anode half-cycle only to the divalent state. In the cathode half-cycle of alternating current, due to the low value of the overvoltage of ion recovery, hydrogen gas is released on the surface of the iron electrodes. Moreover, due to the negative value of the potential of the $\text{Fe}(\text{II}) \leftrightarrow \text{Fe}^0$ system, the reverse cathodic reduction of iron ions (II) to the state of elements does not occur. The processes are repeated at a frequency of 50 Hz in cycle. Thus, in

each anode half-cycle, iron electrodes dissolve according to the reaction (1).

A sulfate solution containing ferrous ions formed in the first electrolyzer (1) was fed into the anode space of the second electrolyzer (2), in which an MA-40 anion exchange membrane separated the electrode spaces. The membrane serves to prevent the reverse reduction of iron ions (III) at the cathode. On the surface of the anode from lead, ferrous ions are oxidized to a trivalent state:



The results of iron oxidation in the first electrolyzer were monitored by determining the weight loss of the iron electrodes. In the second electrolyzer, the amount of iron ions (III) formed was determined by the photocolometric analysis method [15]. The dependences of the decrease in the mass of the iron electrodes upon polarization by alternating current, and the current efficiency of their dissolution on the current density in the first electrolyzer (Fig. 2) and the dependence of the oxidation degree of iron ions (II) to iron ions (III) on the current density upon polarization with the direct current in the second electrolyzer are established (figure 3).

When the current density changes within 80–400 A / m^2 , an almost rectilinear increase in the mass of iron is observed, which transferred to the solution as Fe^{2+} ions (Fig. 2, curve 1). The current efficiency (curve 2) is close to 100%, and sometimes exceeds 100%, since the chemical dissolution of iron in sulfuric acid also occurs simultaneously:

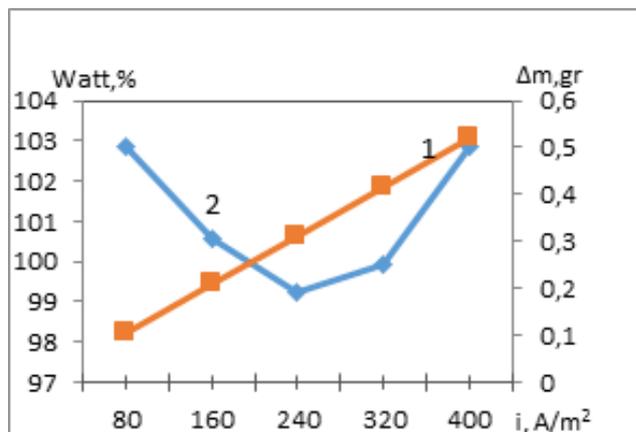
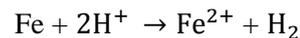


Figure 2 The effect of the current density on the mass of the iron electrodes decrease (curve 1) and the current efficiency (curve 2) when polarized by alternating current ($\tau = 1$ hour; $\text{H}_2\text{SO}_4 = 200 \text{ g} / \text{dm}^3$).

Additional experiments were performed without current polarization with the same

electrodes. It was found that at room temperature in sulfuric acid with a concentration of 200 g / dm^3 , the iron electrodes are dissolved chemically and within 30 minutes, the mass loss of the two electrodes does not exceed 0.0012 g, i.e. 1.2 mg. In this case, the concentration of sulfuric acid has a slight effect on the change in mass of the electrodes (Table).

A table Change in the mass of iron electrodes when dissolved in the sulfuric acid depending on its concentration with no current imposing

$\text{H}_2\text{SO}_4, \text{ g/dm}^3$	50	100	150	200
$\Delta m, \text{mg}$ (1-electrode)	0,3	0,4	0,5	0,6
$\Delta m, \text{mg}$ (2-electrode)	0,3	0,4	0,5	0,6

The sulfate solution obtained in the first electrolyzer is noted to be subjected to evaporation in order to obtain iron sulfate (II) as may be required. The testing carried out in the second electrolyzer with the same mass of Fe^{2+} ions provided that even at a current density of 120 A / m^2 for 1 hour more than 90% of iron (II) goes into the trivalent state. A change in the current density to 600 A / m^2 leads to an increase in the oxidation state to 97.5%, i.e. iron ions (II) are almost completely oxidized under the indicated conditions (Fig. 3). This is apparently due to the fact that, with an increase in the current density at the electrodes, according to the Tafel equation, the anode potential shifts in a more positive direction, i.e. more favorable conditions are created for the oxidation of iron (II).

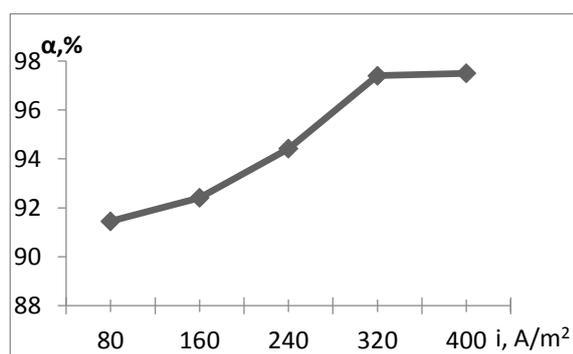


Figure 3 Influence of the tocan density on the degree of iron oxidation (II) being polarized by direct current ($m\text{Fe}^{2+} = 104,1 \text{ mg}$, $\tau = 1 \text{ hour}$)

As the studies provide, an increase in the density of the token electrodes leads to an increase in the rate of the reaction, and accordingly, the efficiency of the process is intensified. We note that

by adjusting the current density in the first electrolytic cell, respectively, in the second electrolytic cell, it is possible to control the rate of formation of the target product.

The sulfate solution containing iron ions (III) was evaporated after electrolysis to form a viscous pasty mass (according to the procedure described in [10]), while its temperature reaches 120°C . The mass was cooled to $45\text{-}50^\circ\text{C}$, the precipitated crystals were sucked off on a Buchner funnel and dried at a temperature of 65°C . The obtained crystals were identified by X-ray phase analysis (Fig. 4), X-ray fluorescence (Fig. 5) and chemical analysis. It was found that the composition of the compound corresponds to the formula: $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

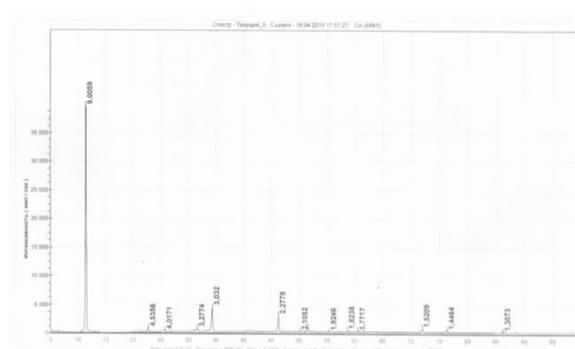


Figure 4 X-ray diffraction pattern of iron sulfate (III)

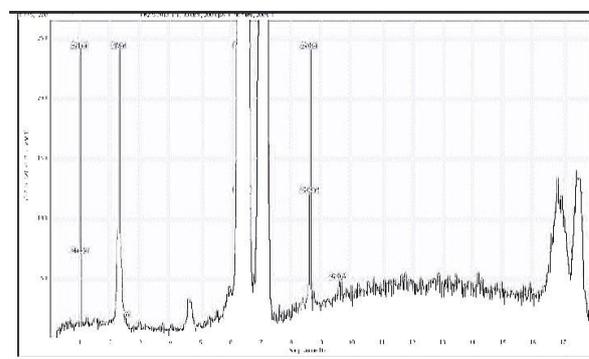


Figure 5 X-ray fluorescence analysis of iron sulfate

Summarizing the results of testing, when the iron electrodes being polarized with the alternating current, the iron was found to be oxidized to a divalent state, and iron sulfate (II) is formed in the solution. With further polarization of the resulting solution by direct current, the iron ions (II) are oxidized to a trivalent state. Based on the results of the study, an electrochemical method for producing iron sulfate (III) was developed [16]. A patent of the Republic of Kazakhstan for a utility model defends the method. The differences and the advantages of the proposed method are that debris, scraps of iron, which are wastes from various technological

processes are used as the feedstock. There is no need to grind metal, making the process easier. The process takes place at room temperature; working conditions are improved, because there is no electrolyte vapor. In addition, there is no need to use nitric acid, respectively, the harmful effects of toxic gas - nitrogen dioxide on the environment are eliminated, and the target product is not contaminated with the nitrate anions.

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Стационарлы және стационарлы емес токтармен поляризациялау кезінде темір сульфаттарының түзілуі

Баешова А. К., Баешов А., Жұмабай Ф. М., Шакенова М. Ш.

Түйіндеме. Темірдің тотығу процесі стационарлы және стационарлы емес электрохимиялық поляризация әдісімен күкірт қышқылды электролиттерде зерттелді. Ең алдымен темір электродтарының тотығуы бірінші электролизерде айналымы ток әсерімен жүргізілді. Темірдің бірінші электролизерде тотығуының нәтижелері темір электродтарының массаларының азаюымен бақыланды. Ток тығыздығы 80-400 А/м² аралығында өзгерген кезде, ерітіндіге Fe²⁺ түрінде өткен темірдің массасы тік сызықты тәуелділік бойынша өзгеретіні анықталды. Ток бойынша шығым 100% -ке жақын, ал кейбір кезде 100%-тен асады, себебі бір уақытта темірдің күкірт қышқылында еруі де орын алады. Бұл ерітіндіні буландыру арқылы темір (II) сульфатын алуға болады. Осыдан кейін құрамында темір (II) иондары бар күкіртқышқылды ерітінді екінші электролизерге жіберілді. Бұл электролизерде темір (II) иондарын темір (III)-ке дейін тұрақты ток әсерімен тотықтыру жүргізілді. Электродтық кеңістіктер МА-40 мембранасымен бөлінді. Екінші электролизерде ток тығыздығы 120 А/м² болғанда 1 сағат ішінде темір (II) иондарының 90%-і үш валентті күйге өтетіні көрсетілді. Ток тығыздығын 600 А/м²-ге дейін өзгерткенде, тотығу дәрежесі 97,5%-ке жетеді, демек, бұл жағдайда темір (II) иондары толық дерлік тотығады. Жүргізілген эксперименттер нәтижесінде темір (III) сульфатын алудың электрохимиялық әдісі жасалды.

Түйінді сөздер: темір, электролит, сульфат, электролиз, айналымы ток.

Формирование сульфатов железа при поляризации стационарными и нестационарными токами

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Аннотация. Методом электрохимической поляризации стационарными и нестационарными токами изучен процесс окисления железа в серноокислых электролитах. Вначале в первом электролизере проводили окисление железных электродов под действием переменного тока. Результаты окисления железа в первом электролизере контролировали путем определения убыли массы железных электродов. Установлено, что при изменении силы тока в пределах 0,1-0,5 А наблюдается практически прямолинейное увеличение значения массы железа, перешедшего в раствор в виде ионов Fe²⁺. Выход по току близок к 100%, а иногда превышает 100%, так как происходит параллельно и химическое растворение железа в серной кислоте. Выпариванием раствора можно получить сульфат железа (II). После этого серноокислый раствор, содержащий ионы железа (II), отправляли во второй электролизер, в котором проводили окисление железа (II) до железа (III) под действием постоянного тока. Электродные пространства были разделены анионитовой мембраной МА-40. Показано, что во втором электролизере при силе тока, равной 0,1 А, в течение 1 часа более 90% железа (II) переходит в трехвалентное состояние. Изменение силы тока до 0,5 А приводит к увеличению степени окисления до 97,5%, т.е. ионы железа (II) практически полностью окисляются в указанных условиях. В результате проведенных экспериментов разработан электрохимический способ получения сульфата железа (III).

Ключевые слова: железо, электролит, сульфат, электролиз, переменный ток.

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Study of the influence of fine fillers from technogenic waste and chemical additives on the properties of self-compacting concrete

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Abstract: The article is devoted to the researches considering the influence of various chemical additives and fine fillers (industrial wastes) available in the Republic of Kazakhstan on concrete mixes and concrete rheological and physical-technical properties. The article provides laboratory studies results of some of self-compacting concrete (SCC) mixtures properties. There were identified the most efficient type of fine-dispersed filler and the most optimal type of chemical additive to be able to get a high-quality SCC mix and a concrete with the class of B25 based on local raw materials. There were enlisted compositions of SCC with a high strength in early terms. The research results are of practical value in the forms of economic efficiency and quality improvement in the production of SCC mixes for manufacturers of ready-mixed concrete operating in the Republic of Kazakhstan.

Keywords: workability, conservability, concrete strength, chemical additives, self-compacting concrete, fine aggregate.

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Introduction

Modern construction requires a variety of building materials with different property complexes. In this regard, high hopes are associated with the improvement of self-compacting concrete (SCC) technology, a material that will soon be widely used in the construction industry of the Republic of Kazakhstan [2]. In recent years, in construction

practice abroad, during the production of new-generation concrete, the development of DMS compositions, which is a material that can be compacted under the influence of its own weight, filling the form even in densely reinforced structures, has become more and more inclined to [3]. This type of heavy concrete has a great future in monolithic construction, prefabricated concrete production, reinforcement of concrete and reinforced concrete

structures for various purposes, as the use of this type of concrete allows you to abandon the traditional paving of concrete with the use of vibrocompaction, optimize labor costs and improve sanitary and hygienic working conditions [2]. SCC is the subject of research by scientists from all over the world. At the moment, there are studies that prove the possibility of creating a high performance SCC with high physical and technical characteristics, as well as the possibility of successful application of fibre reinforcement and application of various industrial wastes [4-6]. The use of SCC greatly reduces the impact of noise pollution on people and the environment during construction, allowing for concrete work in densely populated urban areas and even at night. However, such a sharp difference of the SCC from the traditional classical heavy concrete with the given physical and technical properties poses a number of serious problems to the researchers in the field of concrete science, which require a systematic and step-by-step approach to the prediction of the properties of the SCC, description of the rheological properties of cast concrete mixtures, the optimal distribution of fillers in the concrete matrix, as well as the establishment of dependencies that assess the impact of fine-graded fillers on the characteristics of self-compacting mixtures. Thus, a systematic approach is needed to predict and regulate its properties depending on the tasks set before the researchers [7]. During the construction process, there is a problem of easy paving of concrete mix, which affects the labor costs, timing and cost of construction. In this regard, it is necessary to use a new generation of chemical additives. Chemical additives provide an increase in the decidability of concrete mix, stability to stratification; increase the structural homogeneity of concrete and its strength at an early age of hardening. In addition, according to Professor V.I. Kalashnikov, one of the ways to solve the abovementioned problems is to provide high expansion¹ of coarse aggregate grains. It is impossible to solve this problem by additional application of chemical additives, as it will lead to separation of concrete mixture, and application of fine-dispersed filler gives positive result, especially as it does not lead to loss of durability of SDS in comparison with usual concrete [8]. The purpose of the conducted scientific researches was to study the influence of finely dispersed micro-fillers and various types of chemical additives on rheological and physical-technical properties of the SCC.

Research methods

This paper uses theoretical and empirical research methods. Theoretical research was carried out in order to get acquainted with the existing compositions of concrete mixtures of DMS, to determine the direction of work, to focus on the use of components that are industrial wastes. The empirical studies were aimed at experimental confirmation of theoretically developed composition and methods of SDS production.

The workability (mobility) and stability of concrete mixtures were determined according to [16]. According to this standard, the mobility of the concrete mixture is estimated by the sediment of cone (hereinafter – SC) molded from the concrete mixture. The standard Abrams cone is used. The SC of the concrete mixture is determined twice. The total test time from the beginning of filling the cone with the concrete mixture at the first determination to the moment of SC measurement at the second determination should not exceed 10 minutes. Moreover, the SC of the original sample concrete mixture shall be calculated with rounding to 1.0 cm as the arithmetic mean of the results of the two determinations, which differ from each other for not more than:

- 1 cm for cone draught up to and including 9 cm;
- 2 cm with a cone draft of 10 to 15 cm;
- 3 cm for cone draught of 16 cm or more.

If the difference is higher than the aforementioned, the test is repeated on a new batch of concrete of the same composition. The stability of the concrete mixture is determined by the establishment of mobility at certain intervals from the time of preparation of the mixture [16].

The standard Abrams cone is used to determine the cone melt of the self-compacting concrete. The cone and the metal sheet are wetted, and then the cone is placed on the metal sheet with a smaller base to the sheet surface. The concrete mixture is poured until the cone is completely filled in one step. The cone is lifted within 5-7 seconds, and after the mixture has stopped completely, the two largest melt diameters are measured. The arithmetic mean of the two largest melt diameters is the result of a test.

This study was conducted in four stages, each of which was aimed at solving a specific problem (Fig. 1).

¹ Grain expansion coefficient is the ratio of the volume of the mortar part of the concrete mixture to the volume of voids between the coarse aggregate grains

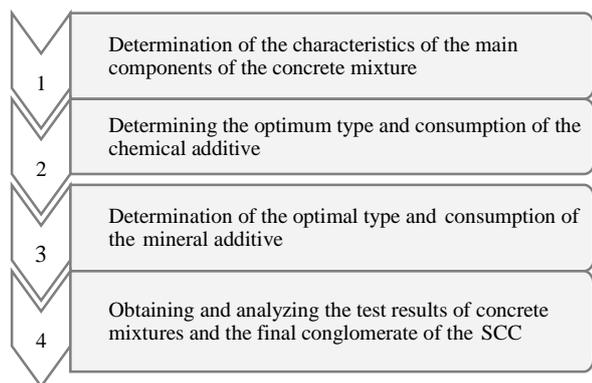


Figure 1 Stages of work

The research methodology is aimed at comparing the rheological and physical-technical characteristics of the concrete mixture obtained as a result of mathematical planning of the experiment by varying the components of the DBMS. All researches and tests were carried out according to the normative documentation operating in the territory of the Republic of Kazakhstan.

Input materials

Local raw materials were used in the work, as well as fine-graded fillers made of waste from the Kazakhstan industry, and a number of chemical additives proposed by Ariranggroup were studied as hyperplasticizers.

M400D20 cement produced by Semey Cement Plant LLP (Semey, Kazakhstan) was used as a binder for the concrete mixtures under study. To confirm the compliance of the selected binder with the norms and requirements [9] a number of tests were conducted. The methods specified in these standards allow to define the following parameters of the building material:

1) Grinding fineness:

The binder under study showed a grinding fineness of 94.4%.

2) Normal density and setting time of cement dough:

The binder under test showed a normal density of 27.30 %. The cure started after 2 hours and 11 minutes, and the cure ended after 4 hours and 10 minutes of cure. These values are included in the normalized area.

3) Compressive and bending strength (at the age of 28 days):

In determining the strength characteristics of the investigated binder showed the result at the age of 28 days: bending - 5.6 MPa; compression - 42.4 MPa. These parameters are included in the normalized area.

For carrying out of tests the sand of the manufacturer "Mark" LLP (Almaty region, Kazakhstan), corresponding to the standard document [10] was used. According to this standard, sands with a maximum amount of dusty and clayey inclusions for groups of increased size, large and medium in size of 3%, can be used as fine aggregate for heavy concrete, under the definition of which the SCC will fall under, [10]. However, according to the results of laboratory and production tests [11], in order to obtain satisfactory characteristics of the concrete mixture and the final conglomerate of the DLS it is necessary to use sand, the amount of dusty inclusions in which does not exceed 1.5% [11]. Testing to determine the amount of dusty and clayey inclusions of the sand under consideration was carried out by the method of soaking according to [12]. According to the test results, the content of dusty and clayey inclusions in the sand under study was 1.08%. Also, according to [12] by sieving and determining the grain composition of the aggregate, was determined by a modulus of grain size of the sand under study, which was 2.6. These parameters are acceptable for the use of the investigated aggregate both in heavy concretes and in the DBMS in particular.

As a coarse aggregate, 5-10 mm and 10-20 mm crushed stone produced by KENTAS LLP (Almaty region, Kazakhstan) with known physical and technical characteristics was accepted. This aggregate meets the requirements of the regulatory document [13], which defines the basic requirements for crushed rock from dense rocks, used as a filler for heavy concrete, including the SCC.

The following chapters discuss the steps for determining the types and costs of chemical and mineralogical additives for SDR based on laboratory testing. The effectiveness of the chemical and mineralogical additives is based on the data obtained from the testing of concrete mixtures and the final conglomerate.

Within the limits of the given research laboratory tests of a concrete mix with application of the following additives-hyperplasticizers of manufacture of factory of "Ariranggroup" (Nur-Sultan, Kazakhstan) on conformity to requirements [14] are carried out:

1. Polycarboxylate ether (hereinafter – PCE);
2. Polycarboxylate ether + Lignosulphonate (hereinafter – PCE+Lig);
3. Naphthalene sulfonate (hereinafter – SNF);
4. Naftalin sulfonate + Lignosulphonate (hereinafter – SNF+Lig);
5. Lignosulphonate (hereinafter – Lig).

Experiemental studies

Determining the optimum type and consumption of the chemical additive.

The primary task was to determine the effectiveness of each of the presented chemical additives in terms of the parameters of paving properties and the stability of the concrete mixture. To carry out the tests it was necessary to determine the basic composition, taking the following corrections [15]: the amount of water in all compositions to take equal to 135 kg/m³, mark on the paving of concrete mixtures - P4-P5, the consumption of additives - 1% of the mass of cement. The composition presented in Table 1 below was accepted as a base one:

Table 1 Basic composition [15]

Cement, kg/m ³	Sand, kg/m ³	Crushed stone, kg/m ³	Water, kg/m ³
350	850	1065	135

Table 2 Test results to determine the suitability and stability of the studied compositions

Type of additive	W/C	Cement, kg/m ³	Sand, kg/m ³	Crushed stone, kg/m ³	Additive, kg/m ³	Water, kg/m ³	SC, cm			
							After the production	After 30 minutes	After 60 minutes	After 120 minutes
PCE	0,39	350	850	1065	3,5	135	22	22	21,5	21
PCE+Lig	0,39	350	850	1065	3,5	135	21	21	19	14
SNF	0,39	350	850	1065	3,5	135	17	16	14	11
SNF+Lig	0,39	350	850	1065	3,5	135	19	18	16	12
Lig	0,39	350	850	1065	3,5	135	20	19	17	13

The results of the conducted tests, reflected in Table 2, show that the concrete mixture with the use of PCE chemical admixture has acquired the largest amount of OK, which indicates its best water-reducing capacity in comparison with other

admixtures. It is also worth noting that this mixture also has the best retention rate.

In order to determine the effect of the type of chemical additive used on the paving properties of the self-compacting concrete mixture, a number of experiments had to be carried out.

The aim of the experiment was to obtain a concrete mixture of SCC with the same cone melt according to [18] and to obtain data on the compressive strength of the studied compositions at the age of 1, 3, 7, 28 days. The experiment was carried out on the previously selected composition of SCC within the framework of the research conducted in 2016-2017 by the Scientific Research Institute of Building Materials and Design of NIISTROMPROEKT LLP in order to select the composition of SCC of M350 class B25 for monolithic construction [18].

Table 3 Compositiion of SSC

W/C	Cement, kg/m ³	Sand, kg/m ³	Cr. stone, 5-10 mm, kg/m ³	Cr. stone, 10-20 mm, kg/m ³	Additive, kg/m ³	Silica, kg/m ³
0,3-0,4	500	999	468	252	10,45	50

According to [19], the SCC is classified into three classes of fitability (Table 4).

Table 4 Classification of the SCC according to suitability

Class	The cone's floating, mm
SF 1	550-650
SF 2	660-750
SF 3	760-850

In order to use the SCC in large-size and reinforced structures in order to obtain the required surface quality, the mixture should correspond to SF class 2 in terms of its suitability for laying, and the optimum is the melting of the cone of 68-75 cm. Therefore, [21] achieved a composition with 75 cm melt cone, adhering to the experience of previous studies.

However, in order to obtain results that reflect the effect of the chemical additive only on the properties of the self-compacting concrete and the mixture, adjustments have been made to the composition shown in Table 3: the fine aggregate is excluded, the additive is reduced to 1%.

Based on the results of the tests performed, the results were obtained as shown in Table 5.

Table 5 – Test results of B25 (M350) concrete mixtures to determine the workability of the concrete mixtures

Hyperplasticizer	W/C	Cement kg/m ³	Sand kg/m ³	Cr. stone, 5-10 mm, kg/m ³	Crushed stone, 10-20 mm, g/m ³	Additive, kg/m ³	Water, kg/m ³	Cone's floating, cm
PCE	0,31	550	999	468	252	5,4	170	75
SNF+Lig	0,35	550	999	468	252	5,4	195	75
SNF	0,36	550	999	468	252	5,4	200	75
PCE+Lig	0,33	550	999	468	252	5,4	180	75
Lig	0,34	550	999	468	252	5,4	190	75

Table 5 shows that:

- when introducing PCE into the concrete mixture of the SCC, the desired characteristics of 75 cm cone melting can be obtained with the lowest water consumption for mixing the mixture;

- Concrete mixture with SNF has the highest water-cement ratio at 75 cm cone floating.

To obtain a complete picture of the influence of the additives under study on the characteristics of the final conglomerate of the SCC, tests were carried out in this paper to determine the compressive strength of the concrete compositions examined in Table 5. The results are shown graphically in Figure 2 below.

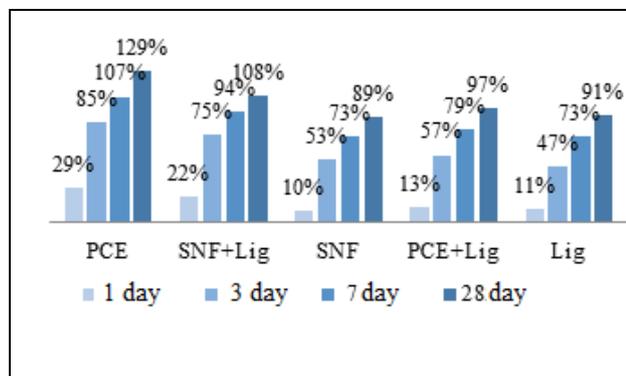


Figure 2 Influence of chemical additives on the strength of concrete mix

If we consider the results of these studies in relation to the production of construction works, then, according to generally accepted methods [22], further loading of reinforced concrete structures can be made at the acquisition of strength of concrete at the rate of 70% of grade strength. Based on the results obtained, it is possible to give a high estimation of the effect of the RSE hyperplasticizer in the SCC. Thus, at the age of 3 days, this composition is gaining strength in the amount of 85% of the grade strength of concrete (B25), which will accelerate the pace of construction work. The highest index of strength at the age of 7 days (107%) and 28 days (128%) is also observed in the composition with the use of RFE. This effect is expected, as the application of RCE has caused the lowest water-cement ratio in the mixture. From which it can be assumed that the basic law [23] of concrete strength (the relationship between strength and water-cement ratio) in this case is not broken and works similarly in the SCC.

Determination of the optimal type and consumption of the mineral additive. The influence of fine aggregate on the properties of concrete was studied by many foreign scientists, the results of which can be used to conclude that micro-fillers affect the hydration of cement, and therefore the properties of self-compacting concrete mixture as a whole [21].

In order to determine the efficiency of application of fine mineral additives made of technogenic waste, similar to the previous tests were carried out in order to obtain concrete mixtures with the same spraying of cone (75 cm) and to determine the strength characteristics of concrete in different curing terms (3, 7 and 28 days).

As a fine-graded filler in this paper we considered:

- Microsilica of Tau-Ken Temir LLP (Karaganda, Kazakhstan);

- Slag of refined ferrochrome (hereinafter - Slag RFH) of JSC "Aktobe Ferroalloy Plant" (Aktobe, Kazakhstan);

- Fly ash from Almaty CHPP-1 (Almaty, Kazakhstan).

In addition to strength characteristics, the influence of the type and quantity of the mineral additive on the stability of the concrete mixture of the SCC with the use of hyperplasticizer PCE was considered.

In order to analyze the efficiency of mineral additives based on production wastes, the compositions of mixtures have been developed in order to obtain 75 cm cone melt. The compositions are presented in Table 6 below.

Table 6 Compositions of concrete mixtures of SCC

Component name	Quantity	Composition number				
		1	2	3	4	5
Cement	kg/m ³	385	385	495	459	477
Microsilica		0	0	55	51	53
Fly ash		0	165	0	0	0
Slag		165	0	0	0	0
Water		160	180	165	160	160
Sand		960	800	999	943	900
Crushed stone 5-10		438	550	468	472	489
Crushed stone 10-15		292	315	252	328	326
Additive PCE		16,5	16,5	16,5	15,3	15,9

The previously described methods [16, 19] have determined the characteristics of the cone melting stability of the concrete mixtures under study. Test results are shown in Fig. 3.

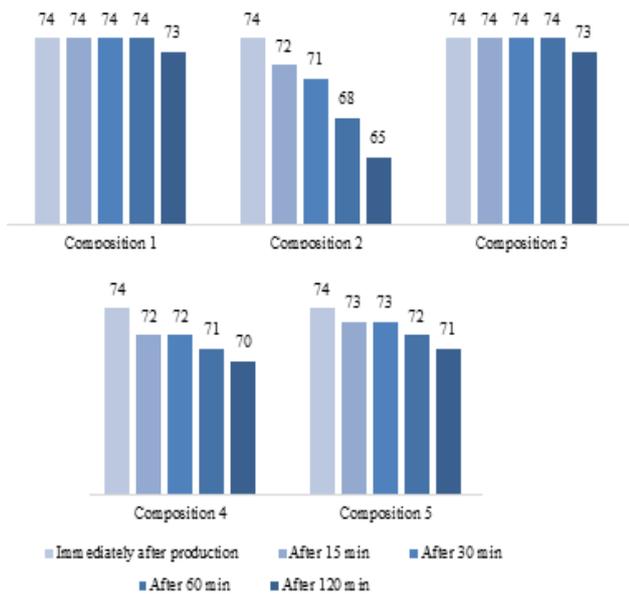


Figure 3 Cone floating and persistence of concrete mixtures of different compositions, see

After the above characteristics were determined, cube samples with a rib length of 150 mm were formed (Fig. 4). Further, the test for determining the compressive strength of cubes at the age of 3, 7 and 28 days of hardening under normal conditions was carried out. The results are shown in Fig. 5.



Figure 4 Concrete cube samples

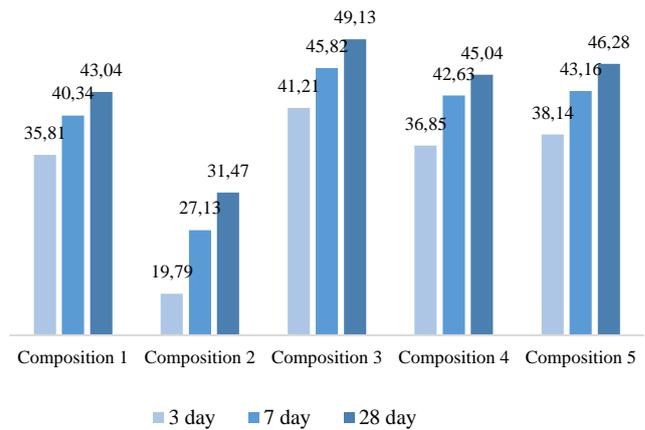


Figure 5 Strength characteristics of the studied compositions, MPa

Discussion of research results

Based on the results of the tests performed, the following can be assumed:

- the mixture with the inclusion of fly ash has the highest water requirement, which affects the strength characteristics of the final conglomerate (the lowest strength of the presented compositions) and the reduction of the mixture persistence;
- the highest strength index shows composition 3 with inclusion of microsilica and the highest cement content, however, this consumption has no effect on the stability of the mixture.

Thus, slag and microsilica are considered acceptable for use. However, it is the microsilica that should be used to obtain the high strength characteristics of the SCC.

Conclusion

Studies have shown that the use of hyperplasticizers based on PCE polycarboxylate esters gives the following effect:

- maintaining the mobility (workability) of the concrete mixture for 2 hours from the time of manufacture.

– the strength of concrete is 107% for 7 days.

When using RFC slag as a micropolluting agent, it is possible to obtain the required shrinkage capacity at $W/C=0.41$, with satisfactory retention and high strength at early curing times.

When using fly ash, the test results are comparatively worse - a decrease in the cone melt in time is observed. Despite the high water-cement ratio of 0.47, the conglomerate strength in the early curing time is much lower than that of other studied compositions.

At introduction in structures of the various maintenance of microsilica, the concrete mix and concrete with the expense of cement 495 kg and microsilica in quantity of 55 kg/m^3 possesses the best characteristics. This composition has the highest strength characteristics at the age of 3 days, as well as a satisfactory preservation of the mixture at a water-cement ratio of 0.33.

Concretes with the use of hyperplasticizers based on PCE polycarboxylates and fine fillers based on microsilica and RFC slag can be classified as "highly-productive" [24], which have high transportability and patchability at the stage of freshly prepared mixture, and in the hardened form – a fast set of strength.

From the received data it is possible to draw a conclusion that for reception of a set of durability of SUB in early terms (for example, 2 days), builders should resort along with increase in the expense of

cement to following technological receptions, such as introduction in structure of concrete of fine-dispersed fillers (microsilica and slag RFH), and also decrease in a water-cement parity by introduction of high enough quantity of the chemical additive on the basis of polycarboxylates PCE. If it is necessary to reduce the consumption of astringent introduction of microsilica or similar mineral additives allows to preserve the physical and technical characteristics of conglomerate [25, 26].

As a whole, it is necessary to note that the purpose of work and the set tasks have been successfully realized, the necessary results for successful practical application have been received.

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Өндірістік қалдықтар мен химиялық қоспалардан бөлінген толтырғыштардың өздігінен тығыздалатын бетонның қасиетіне әсерін зерттеу

Е.Б. Утепов, Д.А. Ахметов, И.Т. Ахматшаева, Е. Н. Роот

Түйіндеме. Мақала Қазақстан Республикасында қол жетімді әр түрлі химиялық қоспалар мен майда бөлінген толтырғыштардың (өндірістік қалдықтардың) бетон қоспалары мен бетонның реологиялық және физикалық-техникалық қасиеттеріне әсерін зерттеуге арналған. Мақалада өздігінен тығыздалатын бетон қоспаларының (ӨТБ) кейбір қасиеттерін зертханалық зерттеу нәтижелері келтірілген. Жергілікті шикізаттан В25 класының жоғары сапалы өздігінен тығыздалатын және бетон қоспасын алуға арналған тиімді бөлінген толтырғыштың және химиялық қоспаның оңтайлы түрі анықталды. Беріктендірудің алғашқы кезеңдерінде жоғары беріктігі бар өздігінен тығыздалатын бетонның композициясы келтірілген. Жұмыстың нәтижелерінің Қазақстан Республикасының аумағында жұмыс істейтін дайын бетон өндірушілер үшін практикалық маңызы бар.

Түйінді сөздер: жұмыс қабілеттілігі, қасиеттердің сақталуы, бетонның беріктігі, химиялық қоспалар, өздігінен тығыздалатын бетон қоспасы, ұсақ дисперсті толтырғыш.

Исследование влияния мелкодисперсных наполнителей из техногенных отходов и химических добавок на свойства самоуплотняющихся бетонов

Е.Б. Утепов, Д.А. Ахметов, И.Т. Ахматшаева, Е. Н. Роот

Аннотация: Статья посвящена исследованиям, рассматривающим влияние различных типов химических добавок и мелкодисперсных наполнителей (техногенных отходов), имеющихся в Республике Казахстан, на реологические и физико-технические свойства бетонных смесей и бетона. В статье приводятся результаты лабораторных исследований некоторых свойств самоуплотняющихся бетонных смесей (СУБ). Выявлен наиболее эффективный вид мелкодисперсного наполнителя и оптимальный тип химической добавки для получения высококачественной смеси СУБ и бетона класса В25 на местных сырьевых материалах. Приведены составы СУБ с высоким набором прочности в ранние сроки твердения. Результаты проведенных работ представляют практическую ценность для заводов-изготовителей товарного бетона, действующих на территории Республики Казахстан.

Ключевые слова: Удобоукладываемость, сохраняемость, прочность бетона, химические добавки, самоуплотняющаяся бетонная смесь, мелкодисперсный наполнитель.

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Calcium nitrate generating out of nitrogen-acid solutions after breaking up slurries of titanium production

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Abstract: This article provides the results of studies of qualitative, quantitative and material composition of titanium production slurry, which is man-made waste. The leaching of slurry parameters by nitric acid are studied: concentration, solid to liquid ratio, temperature and time. The effective leaching parameters were determined: 1.7 mol/l of nitric acid concentration, solid to liquid ratio = 1:8, pH<1, temperature 20±5 °C, leaching time is 30 minutes. The rate of filtration was 0.035-0.044 m³/ m²·h. A gradual leaching method was used to improve the solutions filtration. At the beginning, the slurry was leached with a 0.5 mol/l HNO₃ solution at room temperature for 10 min at solid to liquid ratio = 1:10, the filtration rate was 0.062 m³/ m²·h. Then the cake was again leached with 3.5 mol / l HNO₃ at room temperature for 30 min at solid to liquid ratio = 1:10, the filtration rate was 0.094 m³/ m²·h. Calcium hydroxide or lime milk was selected as the reagent to precipitate impurities out of solutions. The content of impurities of iron, titanium and aluminum is significantly reduced when 2.8-5 pH values. The best purification of calcium nitrate solutions by lime milk was at pH 8. Calcium nitrate crystals were obtained by evaporation of a purified solution of 8 pH value out of a slurry leaching when 5% ammonium nitrate was added to it by weight of Ca(NO₃)₂. The dehydrated calcium nitrate was obtained by granulating 92-95% of the melt in the form of flakes at 90 °C of a surface temperature of the granulator plate.

Keywords: leaching, chloride waste, nitric acid, filtration, precipitation, calcium nitrate, crystallization, granulation.

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Introduction

The titanium sponge production by magnesium thermal reduction of titanium tetrachloride at 850 °C involves the production of magnesium metal by electrolysis from its molten salts [1]. The raw material for the production of magnesium electrolysis is dehydrated carnallite, and the spent electrolyte is used in the chlorination of

titanium slurries. At the stages of titanium slurry chlorination and magnesium electrolysis, a significant amount of chloride wastes is generated.

These industrial wastes pose a danger to the environment, polluting soils and natural waters when they are released into the atmosphere, when industrial wastewater is discharged into the waters, and when solid wastes are stored in the slurry storages [2].

The Institute of Metallurgy and Ore Benefication JSC (IMOB), along with the Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UKTMP), has been conducting researches to process chloride titanium-magnesium wastes for several years.

In [3,4] the results of synthetic carnallite generating studies out of worked out molten titanium chlorinator (MTC) and magnesium slurries are presented. Slurries were leached with water, the solution was purified, and a solution with a carnallite module $KCl/MgCl_2 = 0,8-1,0$ was obtained by combining the saline solutions. The resulting saline solution was g/dm^3 : Ti 0.0001-0.0004; Fe 0.001-0.003; Si 0.026-0.033; Mn 0.04-0.06. A carnallite that meets the State Standard 16109-70 requirements was obtained by evaporation and crystallization out of solution. In [5], the results of studies of REE concentrate extraction out of MTC are provided. The through recovery of the rare earth elements out of MTC into collective concentrate was 66%. The developed method [6] for extracting niobium from PC sublimates involves their leaching with a solution of sulfuric acid, chloride distillation of cakes, and hydrolytic treatment of sublimates to obtain niobium-containing intermediate product [7].

Each year UKTMP JSC produces 30-35 thousand tons of solid chloride wastes containing 700-1400 tons of titanium oxide. Some titanium chloride wastes are leached with water and neutralized with calcium hydroxide to 7-8.5 pH. The resulting pulp is pumped to the slurry collectors and accumulated in them. Reserves of sediments or slurries are about 320 thousand tons, the multicomponent composition of which is present in the form of oxides, oxychlorides and carbonates [8]. Titanium slurry is a man-made raw material that is stored in the slurry collectors. Retrieving valuable products out of it is an urgent task. Currently, IMOB JSC is developing a technology for processing titanium slurry. An objective is to study the process of slurry leaching with nitric acid, purification of the obtained slurries from impurities, evaporation of solutions and calcium nitrate crystallization.

Testing and discussing results

The titanium slurry was crushed, aggregated and dried before the physicochemical studies, since its humidity was 30%. The chemical composition of the slurry, wt. %: 6.82 Ti, 2.78 Fe, 19.4 Ca, 2.19 Al, 0.48 S, 8.19 Si, 0.13 V, 0.32 Nb, 7.09 C.

Methods of analysis. X-ray phase analysis of the slurry was carried out using D8 Advance diffractometer (BRUKER), Cu $-K\alpha$ radiation, the

results are provided in Table 1. The samples were decrypted and the phases were searched with the help of the Search / match program using the ASTM Card Database.

Table 1 – A slurry phase composition

Compound Name	Formula	S-Q, %
Calcite	Ca(CO ₃)	31,33
Vaterite, syn	Ca(CO ₃)	13,88
Quartz, syn	SiO ₂	12,37
Sulfur, syn	S ₈	7,18
Hydrogen Titanium Oxide	H ₂ Ti ₃ O ₇	6,90
Titanium Oxide	Ti ₆ O ₁₁	6,05
Hydrocalumite, syn	Ca ₄ Al ₂ O ₆ Cl ₂ 10H ₂ O	5,38
Portlandite, syn	Ca(OH) ₂	4,97
Rutile, syn	TiO ₂	4,45
Titanium Aluminum Niobium Oxide	Ti _{0.8} Al _{0.1} Nb _{0.1} O ₂	3,98
Akermanite, aluminian, syn	Ca ₂ (Al _{0.46} Mg _{0.54}) (Al _{0.23} Si _{0.77}) ₂ O ₇	3,51

Effect of nitric acid concentration. Slurry leaching was carried out at different concentrations of nitric acid, studying the dynamics of the degree of titanium and calcium extraction into the solution.

The testing methods. The experiments were carried out under the following condition: a slurry weight is 50 g; solid to liquid ratio = 1:4, temperature is 20 °C, within 30 minutes with a change in acid concentration. Distilled water and 9.1 mol / l nitric acid were added to the glass in the required amount to obtain the necessary concentration with a measurement of the density of the solution. The pulp was mixed with a mechanical stirrer at a speed of 300 rpm. After the experiment, the pulp was filtered, the filtration rate was measured, and then the precipitate was dried and weighed. The volume of the filtrate was measured. The resulting cake and solution products were tested for X-ray fluorescence and chemical analyzes.

The degree of titanium extraction into the solution is closer to zero, with leaching with a concentration of 0.7-1.7 mol / l HNO₃. At the same time, the extraction of calcium into the solution increased from 6.4% at a concentration of 0.7 mol / l HNO₃, and at a concentration of 1.7 mol / l HNO₃ to 52%. A subsequent increase in the concentration of nitric acid led to a gradual transition of titanium into a solution of leachable slurry. With an increase in concentration from 1.7 to 4.5 mol / l HNO₃, titanium recovery gradually increased from 0.2% to 4.9%, and calcium sharply. At 0.5-0.7 mol / l HNO₃, the calcium

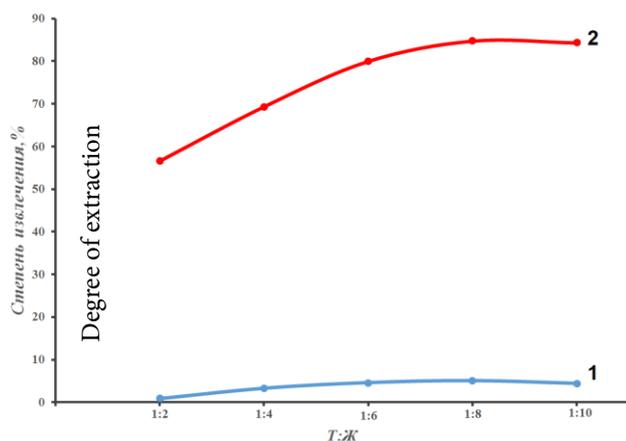
recovery in the solution was 60-64%. The yield of cakes changed with increasing concentration of nitric acid from 46.3 to 29.5%, and the filtration rate decreased from 0.45 to 0.044 m³ / m²·h.

The influence of solid to liquid ratio. Leaching slurry studies out of titanium production at various solid to liquid ratio were carried out at a concentration of 3.5 mol / l HNO₃. This is justified by the fact that at such a concentration there is a maximum extraction of calcium into the solution, as well as a minimum transition of titanium into the solution. The research results are shown in Figure 1. The diagram demonstrates an increase in solid to liquid ratio leads to the increase calcium into the solution extraction, but titanium does not significantly. But with a solid to liquid ratio = 1:10, the extraction of titanium into the solution was 6.2%.

With an increase in solid to liquid ratio, the extraction of calcium in the solution increases sharply, the extraction of titanium in the solution practically does not change. With a solid to liquid ratio = 1:2, calcium extraction into the solution is 56.7%, in cake - 10.6%. The filtration rate was 0.005 m³ / m²·h.

Leaching with nitric acid at solid to liquid ratio = 1:4 provided the extraction into a solution of wt. %: titanium 3.28; calcium 69.3. With a solid to liquid ratio = 1:6, the extraction into a solution of wt. %: titanium 4.57; calcium 79.9; silicon impurities 0.6; iron 28.7; aluminum 36.3. The filtration rate was 0.026 m³ / m²·h.

Leaching at a solid to liquid ratio = 1:8, extraction into a solution of wt. %: titanium 5.04; calcium 84.7. With a solid to liquid ratio = 1:10, the extraction into a solution of wt. %: titanium 4.4; calcium 84.3; silicon impurities 0.73; iron 27; aluminum 39.1. The filtration rate was 0.035-0.044 m³ / m²·h.



1 – titanium; 2 – calcium.

Figure 1. The dependence of the titanium and calcium extraction into a solution on the solid to liquid ratio at 3.5 mol / l HNO₃

With an increase in solid to liquid ratio, the cake yield decreased from 32.2 to 22%, and the filtration rate increased from 0.005 to 0.044 m³ / m²·h.

Leaching with nitric acid at a solid to liquid ratio = 1:10 can be considered more effective in terms of filtration rate and the extraction of calcium in a solution of 84.3%. The loss of titanium with a solution is 4.4%, and with a solid to liquid ratio = 1:8, the loss was 5.04%, the yield of cake is almost the same.

The temperature effect. Experiments about the temperature effect were carried out under the following leaching conditions: 3.5 mol / l HNO₃ at a solid to liquid ratio = 1:8, leaching time 30 minutes. The results of the experiments are provided in Figure 2.

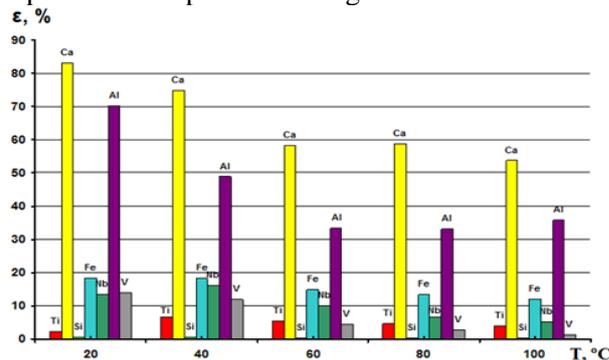


Figure 2. The dependence of the main components extraction into the solution on the temperature of 3.5 mol / l HNO₃

As the Figure 2 provides, the extraction of calcium, iron, and aluminum decreases as the temperature increases due to the formation of gels that impede filtration. PH values ranged from -0.45 to -0.64. The filtration rate decreased from 0.035 to 0.004 m³ / m²·h.

Duration effect: Studies about leaching duration of 3.5 mol/l with the nitric acid were carried out at a temperature of 80 °C with a solid to liquid ratio = 1:8. The results of the experiments are provided in Figure 3.

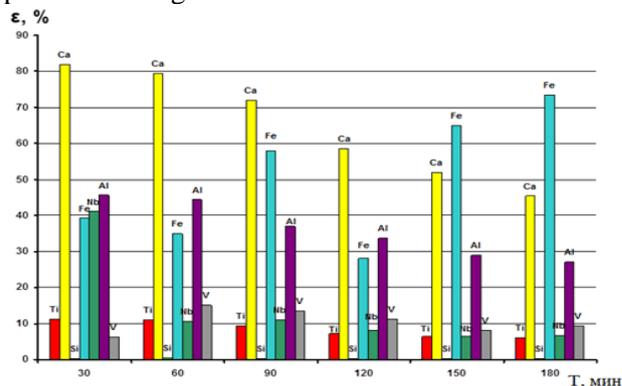


Figure 3 - Dependence of the main components extraction into the solution on the leaching duration at 3.5 mol/l HNO₃

With an increase in the leaching duration, the amount of gel increased the extraction of calcium into the solution decreased from 82 to 45.5%, and the extraction of titanium into the solution also decreased from 11.2 to 5.9%. Filtration was very slow.

When the slurry was leached with 3.5 mol / l nitric acid, the solid to liquid ratio = 1:8, the effective temperature of 20 ± 5 °C and the efficient leaching time of 30 minutes were chosen. With these effective parameters, the extraction in titanium solution was 2.2%, and the extraction in calcium solution was 84.7%, the filtration rate was 0.035-0.044 m³ / m²·h.

However, at concentrations of 2.6-3.5 mol / l nitric acid and temperatures above 60 °C, silicate colloidal compounds are formed into solutions in large quantities, which impede filtration. At a temperature of 20 ± 5 °C, colloidal compounds formed less, but the filtration rate remained low. To improve the filtration of solutions, one of the methods was used [9]. First, the slurry was leached with a 0.5 mol / l HNO₃ solution at room temperature for 10 min at a solid to liquid ratio = 1:10, the filtration rate was 0.062 m³ / m²·h. The filtered cake was again leached with 3.5 mol / l HNO₃ at room temperature for 30 min at a solid to liquid ratio = 1:10, the filtration rate was 0.094 m³ / m²·h.

The next step is the deposition process. Calcium hydroxide or lime milk was selected the reagent for the precipitation of impurities from solutions of calcium nitrate. A 2 liters' solution was obtained by leaching titanium production slurry with nitric acid under the following leaching conditions: 3.5 mol/l HNO₃ concentration, solid to liquid ratio = 1:10, temperature 20 ± 5 °C, leaching time 30 min, stirring speed 300 rpm / min. The composition of the solution, wt.%: 0.72 Ti, 18.1 Ca, 0.047 Si, 1.15 Fe, 0.032 Nb, 1.09 Al, 0.025 V. The green solution with pH value is -0.86. The initial solution in the experiments on the deposition of

impurity components was taken in a certain amount; a solution of lime milk was gradually poured. The conditions of experiments and the composition of the solutions with the addition of lime milk are provided in Table 2.

The experiments resulted in at pH values of -0.56 and 0.03, the main impurities of iron, aluminum, and titanium remain in the solution. At pH values of 2.8-5, the content of impurities of iron, titanium and aluminum is significantly reduced. An increase in the deposition time of impurities also positively affects the cleaning of the solution.

After 5 pH solution was evaporated at a temperature of 100 °C for 4 hours, a viscous amorphous substance was obtained; it was not possible to obtain crystals of calcium nitrate. According to a number of signs, Ca(NO₃)₂ can be attributed to hard-crystallizing salts, its hygroscopic point is very low, calcium nitrate is prone to recrystallization and caking during storage of [10]. For these purposes, 5-7% ammonium nitrate is used by weight of calcium nitrate for better crystallization. With the addition of ammonium nitrate, the crystallization rate of Ca(NO₃)₂ increases 1.5-2 times with a simultaneous increase in the crystallization temperature by 50 °C. The more ammonium nitrate is contained in the solution; the better is crystallization [11]. Therefore, 5% by weight of Ca(NO₃)₂ ammonia and nitric acid was added to the solution to produce ammonium nitrate. But when ammonia was added from the solution, flakes of iron oxide remained in the form of nitrate, the pH of the solution was 8. The composition of the solution, wt.%: N/D Ti, 28.1 Ca, 0.004 Si, 0.001 Fe, N/D Nb, 0.001 Al, N/D V. Crystals of calcium nitrate were managed to evaporate from this solution, their x-ray phase analysis has been provided in Table 3.

Table 2 - The content of solutions when adding lime milk

Test No.	Initial solution, ml	pH of solution	Lime milk, ml	Deposition time, min	Composition, g / dm ³						
					Ti	Ca	Fe	Al	Si	Nb	V
1	200	-0,56	88,5	10	0,44	12,72	0,79	0,67	0,041	0,024	0,035
2	200	0,03	200	10	0,34	19,39	0,52	0,45	0,088	0,011	0,024
3	130	5,0	230	10	0,00012	23,9	0,024	0,16	0,06	-	0,0082
4	100	2,8	85	30	0,00012	31,25	0,0089	0,0086	0,0032	-	0,009
5	100	3,05	95	30	0,00012	30,14	0,0076	0,62	0,088	-	0,0094

Table 3 - Phase composition of calcium nitrate

Compound Name	Formula	S-Q, %
Calcium Nitrate	$\text{Ca}(\text{NO}_3)_2$	71
Calcium Nitrate Hydrate	$\text{Ca}(\text{NO}_3)_2(\text{H}_2\text{O})_2$	29

The composition of the calcium nitrate salt was studied using a JEOL JXA 8230 Electron Probe Microanalyses.

An electron probe study of slurry was carried out in the following modes: 1. COMPO - salt image in the back-scattered electrons; 2. WDS - waveguide dispersive spectroscopy with a sharper and more sensitive image. Figure 4 provides the calcium nitrate zones in the backscattered and secondary SEI electrons.

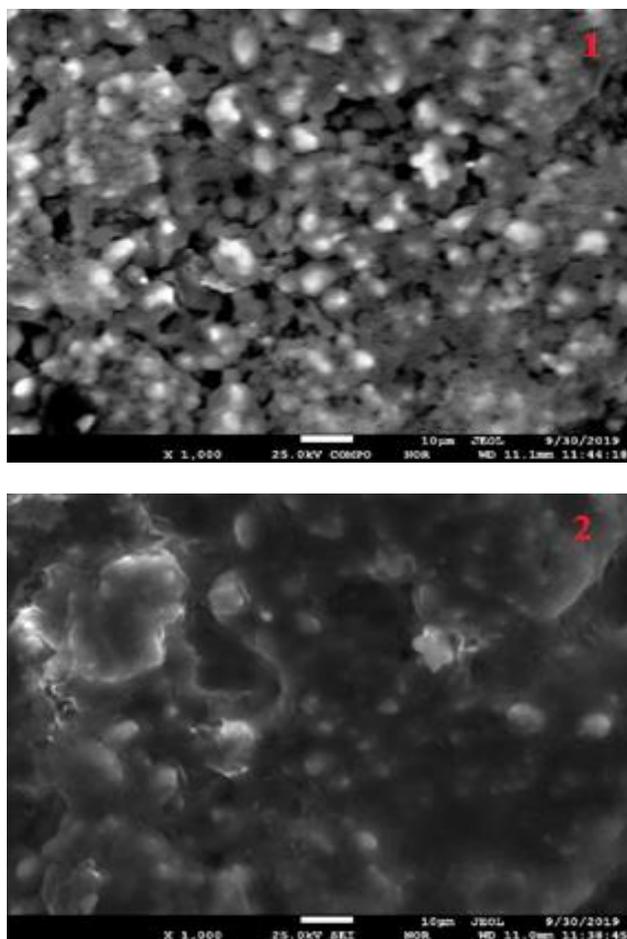


Figure 4 - Calcium nitrate crystals in the COMPO (1) and SEI (2) modes. 1000 zoom

The obtained crystals from the purified solution to pH 8 with the addition of ammonium nitrate in an amount of 5% of the total weight of the obtained calcium nitrate were subjected to grade analysis. Figure 5 provides the results of a sieve

analysis. The +7 mm fraction was 36.2%, the -7 + 5 mm fraction was 14%, the -5 + 3 mm fraction was 15%, the -3 + 1 mm fraction was 18%, and the -1 mm fraction was 16.8%. The main fraction of -3 + 1 mm was 18% of the total weight, the loss was 1.5%.

Grade analysis showed that the more acceptable fractions of -5 + 3 mm and -3 + 1 mm in total amounted to 33%. Large fractions of +7 mm, -7 + 5 mm made up the bulk of the grade analysis of 50.2%.

According to Inter-Republic specifications 6-03 195-67, calcium nitrate for fertilizer is produced in the form of a scaly product. Light brown color. Containing at least 17.5% nitrogen, the content of ammonium nitrate is 4-7%, and the moisture content is not more than 14% [11]. Crystallization of calcium nitrate with the addition of ammonium nitrate on a cooling roll is carried out at 90 °C. Most of the salt crystallizes as a two-water hydrate. The melt temperature in the trough of the rollers is maintained at about 110 °C. Before loading into the container, calcium nitrate should be cooled to at least 30 °C, since hot salt is prone to sticking and impairs its dispersibility. Calcium nitrate is cooled in a drum through which cooled air is blown. At elevated temperatures, calcium nitrate can go into the solid phase as an anhydrous salt.

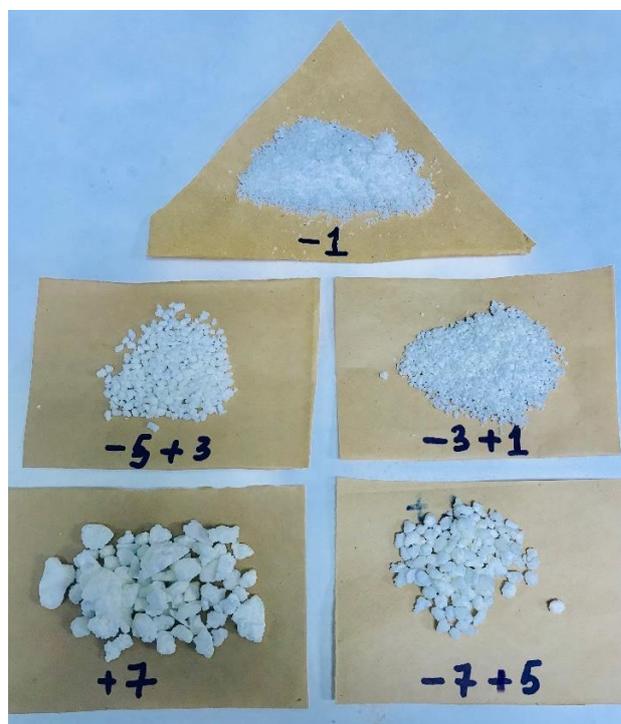


Figure 5 - Fractions of grade analysis when adding 5% ammonium nitrate to the solution

In the first experiment, a saturated solution of 70% concentration of $\text{Ca}(\text{NO}_3)_2$ was prepared and

evaporated to form a melt at 100 °C. The melt was evenly distributed over the granulator plate, which rotated at a speed of 28 rpm. The molten salt of ammonium nitrate began to granulate first into medium-sized granules, but due to the presence of physical moisture, small salt particles began to stick to the granules and granules of 6-8 mm in size formed. The second experiment was also carried out with a saturated solution of 70% concentration of $\text{Ca}(\text{NO}_3)_2$, and it was evaporated to form a melt at 100 °C. Preliminarily, the granulator plate was heated with a gas can to a temperature of 90 °C during rotation of the granulator at a speed of 28 rpm. At elevated temperatures, calcium nitrate can go into the solid phase as an anhydrous salt. The calcium nitrate melt was evenly distributed over the granulator plate, it solidified with an even layer, then it was removed in the form of flakes with a stainless steel scraper, and the granulation results are shown in Figure 6.



Figure 6 - Obtaining flake calcium nitrate using a granulator

Table 4 provides the results of grade analysis of the obtained calcium nitrate. The results of X-ray analysis of calcium nitrate are provided in Table 5.

Table 4 - Grade composition of dehydrated calcium nitrate using a granulator

Grain type of crystals, mm	Grade composition, %
+7	28,2
-7+5	12,7
-5+3	17,5
-3+1	17,5
-1 mm	24,1
Total:	100

Table 5 - X-ray phase analysis of dehydrated calcium nitrate.

Compound Name	Formula	S-Q, %
Calcium Nitrate	$\text{Ca}(\text{NO}_3)_2$	100

A large fraction was crushed to a fraction of -3 + 1, a small -1 mm was sent to receive melt. Thus, dehydrated calcium nitrate was obtained by granulation of 92-95% melt in the form of flakes. We grind a large fraction to a fraction of -3 + 1 mm, and a -1 mm fraction is sent to receive melt.

Conclusion

According to the results of X-ray phase analysis, the main phases of the slurry are calcite 31.33%, vaterite 13.88%, quartz 12.37%; titanium is present in the phases of rutile 4.45%, lower titanium oxide 6.05%, titanium hydrogen oxide 6.9%; calcium is also present in the phases of hydrocalumite 5.38%, portlandite 4.97%, aluminum ackermanite 3.51%, also sulfur 7.18%.

The titanium and calcium distribution was studied at effective parameters of the leaching process: acid concentration, solid to liquid ratio, pH. The effective leaching parameters were determined: 3.5 mol / l nitric acid concentration, solid to liquid ratio = 1:8, $\text{pH} < 1$, the temperature 20 ± 5 °C, leaching time 30 minutes. The filtration rate was $0.035\text{-}0.044 \text{ m}^3 / \text{m}^2\cdot\text{h}$.

To improve the solutions filtration, the following method was applied. First, the slurry was leached with a 0.5 mol / l HNO_3 solution at room temperature for 10 min at a ratio of solid to liquid ratio = 1:10, the filtration rate was $0.062 \text{ m}^3 / \text{m}^2\cdot\text{h}$. The filtered cake was again leached with 3.5 mol / l HNO_3 at room temperature for 30 min at a ratio of solid to liquid ratio = 1:10, the filtration rate was $0.094 \text{ m}^3 / \text{m}^2\cdot\text{h}$.

Crystals of calcium nitrate were obtained from the purified solution to pH 8 with the addition of ammonium nitrate in an amount of 5% of the total weight of the obtained calcium nitrate. Grade composition of dehydrated calcium nitrate on a granulator, %: type + 7 mm - 28.2; type -7 + 5 mm - 12.7; type -5 + 3 mm - 17.5; type -3 + 1 mm - 17.5, type -1 mm - 24.1. A large fraction was crushed to a fraction of -3 + 1, a small -1 mm was sent to receive melt.

The dehydrated calcium nitrate was obtained by granulating 92-95% of the melt in the form of flakes at a surface temperature of the granulator plate of 90 °C. We grind a large fraction to a fraction of -3 + 1 mm, and a -1 mm fraction is sent to receive melt.

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Титан өндірісіндегі қоқырларды ашу барысында түзілген азотқышқылды ерітінділерден кальций селитрасын алу

Есенгазиев А.М., Ультаракова А.А., Улдаханов О.Х.

Түйіндеме: Техногенді қалдық болып табылатын титан өндірісіндегі қоқырларды шаймалау бойынша зерттеулер жүргізілген. Шаймалауды азот қышқылымен әр түрлі концентрацияда, Қ:С қатынасында, температурада және уақытта жүргіздік. Шаймалаудың оптималды параметрлері анықталған: 3,5 моль/л азот қышқылы концентрациясы, Қ:С=1:8, рН<1, температура 20±5°C, шаймалау уақыты 30 минут. Фльтрация жылдамдығы 0,035-0,044 м³/м² сағ құрады. Ерітіндінің фильтрациясын жақсарту мақсатында шаймалаудың кезендік әдісі қолданылған. Бастапқыда қоқырды 0,5 моль/л HNO₃ ерітіндісімен Қ:С=1:10 қатынасында, бөлме температурасында 10 мин мерзімде шаймаладық, фильтрация жылдамдығы 0,062 м³/м²·сағ құрады. Сосын кекті 3,5 моль/л HNO₃, бөлме температурасында, Т:Ж=1:10 қатынасында, 30 мин мерзімде, тағы да шаймаладық. Фльтрация жылдамдығы 0,094 м³/м²·сағ құрады. Кальций гидроксиді және сұйық әк ерітіндідегі қоспаларды тұндыруда реагент ретінде таңдалды. Ерітіндіде рН 2,8-5 мәнінде темір, титан және алюминий қоспаларының мөлшері азаяды. Кальций нитраты ерітіндісін сұйық әктаспен ең үздік тазалау рН 8 жүзеге асты. Аммоний нитратын алуда Ca(NO₃)₂ салмағынан 5% мөлшерде аммиак және азот қышқылын қоса отырып, рН 8 де тазаланған ерітіндіні буландыру арқылы кальций нитраты кристалдары алынды. Қабыршақ тәрізді сусыздандырылған кальций нитраты 92-95 % балқыманы грануляциялау арқылы алынған. Гранулятор тарелкесі температурасы 90 °C құрады.

Түйін сөздер: шаймалау, хлоридті қалдықтар, азот қышқылы, фильтрация, тұндыру, кальций нитраты, кристаллизация, грануляция.

Получение кальциевой селитры из азотнокислых растворов от вскрытия шламов титанового производства

Есенгазиев А.М., Ультаракова А.А., Улдаханов О.Х.

Резюме: В статье представлены результаты исследований по изучению качественного, количественного и вещественного состава шлама титанового производства, являющийся техногенным отходом. Изучены параметры выщелачивания шлама азотной кислотой: концентрация, соотношение Т:Ж, температура и время. Были определены оптимальные параметры выщелачивания: 1,7 моль/л концентрация азотной кислоты, Т:Ж=1:8, рН<1, температура 20±5 °С, время выщелачивания 30 минут. Скорость фильтрации составила 0,035-0,044 м³/м²·ч. Для улучшения фильтрации растворов был применен поэтапный способ выщелачивания. Сначала шлам выщелачивали 0,5 моль/л раствором HNO₃ при комнатной температуре в течение 10 мин при Т:Ж=1:10, скорость фильтрации составила 0,062 м³/м²·ч. Затем кек вновь выщелачивали 3,5 моль/л HNO₃ при комнатной температуре в течение 30 мин при Т:Ж=1:10, скорость фильтрации составила 0,094 м³/м²·ч. Реагентом для осаждения примесей из растворов был выбран гидроксид кальция или известковое молоко. При значениях рН 2,8-5 в растворах значительно уменьшается содержание примесей железа, титана и алюминия. Наиболее лучшая очистка растворов нитрата кальция известковым молоком была при значении рН 8. Получены кристаллы нитрата кальция выпариванием очищенного раствора со значением рН 8 от выщелачивания шлама при добавлении в него 5 % нитрата аммония от веса Ca(NO₃)₂. Получен обезвоженный нитрат кальция путем грануляции 92-95 % плава в виде чешуек, при температуре поверхности тарели гранулятора 90 °С.

Ключевые слова: выщелачивание, хлоридные отходы, азотная кислота, фильтрация, осаждение, нитрат кальция, кристаллизация.

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Разработка энергосберегающего способа для переработки техногенных отходов

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Резюме. Разработан энергосберегающий способ переработки техногенных отходов – слой расплава с инверсией фаз как комбинация режимов «идеального» смешения и «идеального» вытеснения. На его основе создан плавильный агрегат нового поколения – «реактор инверсии фаз-трубчатая печь». Полученные экспериментальные данные показывают, что в слое инверсии фаз удельный расход топлива на переработку «бедных» по цинку отвальных и «богатых» по цинку шлаков примерно одинаков. Последнее положение противоречит устоявшемуся мнению металлургов, что переработка шлаков с концентрацией цинка менее 5% нерентабельна. Результаты расчетов демонстрируют, в случае внедрения промышленного образца агрегата «реактор инверсии фаз-трубчатая печь» для переработки «бедных» шлаков, по сравнению с вельцевой перерабатывающей «богатый» шлак, удельный расход условного топлива сократится в 1,5-1,7 раза, а удельная производительность возрастет в 1,4-1,5 раза. Промышленная реализация агрегата «реактор инверсии фаз-трубчатая печь» позволила бы рентабельно перерабатывать отвалы шлаков фьюмингования, клинкера вельцевания, «бедные» цинковые руды, хвосты обогащения и других отходов цветной металлургии.

Ключевые слова: энергосберегающий способ, реактор инверсии фаз – трубчатая печь, «бедные» по цинку шлаки, комбинация режимов «идеального» смешения и вытеснения.

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Введение

В Республике Казахстан отходы горно-металлургической отрасли составляет около 20 миллиардов тонн, из них цветной металлургии ~ 10,1, черной - ~ 8,7 миллиардов тонн [1,2]. Содержание ценных компонентов в них не меньше чем в низкопотенциальном минеральном сырье. Извлечение металлов из них нерентабельно, так как требует двухразового повышения удельного расхода топлива, чем из природного «богатого» сырья [3-5]. Согласно данным экспертов разведанные запасы «богатого» сырья достаточно только на 30-35 лет [1,2]. В будущем, истощение запасов «богатых» руд может привести к необходимости

переработки техногенных отходов. Однако в области переработки техногенных отходов, равно как и низкопотенциального сырья, отсутствует конкретное техническое решение позволяющее рентабельно извлечь из них ценные компоненты [6-15]. Последнее обстоятельство стимулирует исследователей к поиску способов и средств позволяющих сократить расход топлива в 2-3 раза по сравнению с существующими процессами.

Методы исследования.

Альтернативным способом достижения этой цели является методология предельного энергосбережения [4,16]. Одним из ее принципов

является разработка энергосберегающего способа, создание на его основе пилотной установки, проведение экспериментов и перерасчет характеристик пилотной установки на промышленный образец методом афинного моделирования.

Результаты экспериментов на пилотной установке

Переработку сырья в расплаве по структуре слоя режиму обработки можно разделить на три основных способа: 1) **барботажный слой**, где структура слоя имеет вид «жидкость – сплошной, газ - дискретный» (рис. 1а); 2) **кипящий слой расплава**, характеризующийся состоянием «газ-сплошной, жидкость-дискретный», по определению относящемуся к режиму «идеального» смешения (рис. 1б) и **слоя расплава с инверсией фаз**, как комбинация режимов «идеального» смешения и «идеального» вытеснения [4,16-21](рис.1в).

Для отбора энергосберегающего способа переработки низкопотенциального техногенного сырья были проведены эксперименты на установке «реактор инверсии фаз-трубчатая печь» с применением традиционного **барботажного слоя** и новых способов обработки шлаков - **кипящего слоя расплава** и **слоя расплава с инверсией фаз** в **непрерывном** режиме [18,19]. Принцип работы установки следующий (рис. 3,4). Процесс непрерывный. Отвальный шлак с бункеров загружается в трубчатую печь, где нагревается до

900⁰С отходящими газами реактора инверсии фаз (РИФ) и затем подается в РИФ для расплавления и отгонки цинка. Обедненный по цинку расплав гранулируется водой и направляется на производство стройматериалов. Отходящие газы трубчатой печи нагревают дутьевой воздух в воздухоподогревателе, затем очищаются от цинковых возгонов в скруббере. При восстановлении только цинка, обеспыленные газы выбрасываются в атмосферу, а в случае восстановления железа, горючие газы используются для технологических целей.

Условные обозначения на рисунке 3: 1 – реактор инверсии фаз, 2 – вращающаяся часть печи, 3 – неподвижная часть печи с теплообменником, для подогрева/пиролиза природного газа, 4 - воздухоподогреватель, 5– пароперегреватель, 6 – коллектор ввода дополнительного природного газа, 7 – шлакозагрузочная труба, 8 – привод трубчатой печи, 9-уплотнение зазоров вращающейся части печи. 10–скруббер, 11 – топка, ПРГ – природный газ, СВС – сажеводородистая смесь подогретого природного газа, ГГ – горючий газ или обеспыленный дымовой газ, Ш – шлак, Р - расплав.

В период проведения экспериментов в режиме «плавка-восстановление» установка проработала около 1000 часов. Было переработано ~250т «бедного» шлака состава: ZnO (3.8 – 4,3); PbO (0.1 – 0.15); Cu (0.6 – 0,8); FeO(7 – 8); Fe₂O₃(2 – 3); Fe₃O₄ (23 – 24); SiO₂(27 – 28); CaO (13 – 14); Al₂O₃(7 – 9); S (0.4 – 0.5).

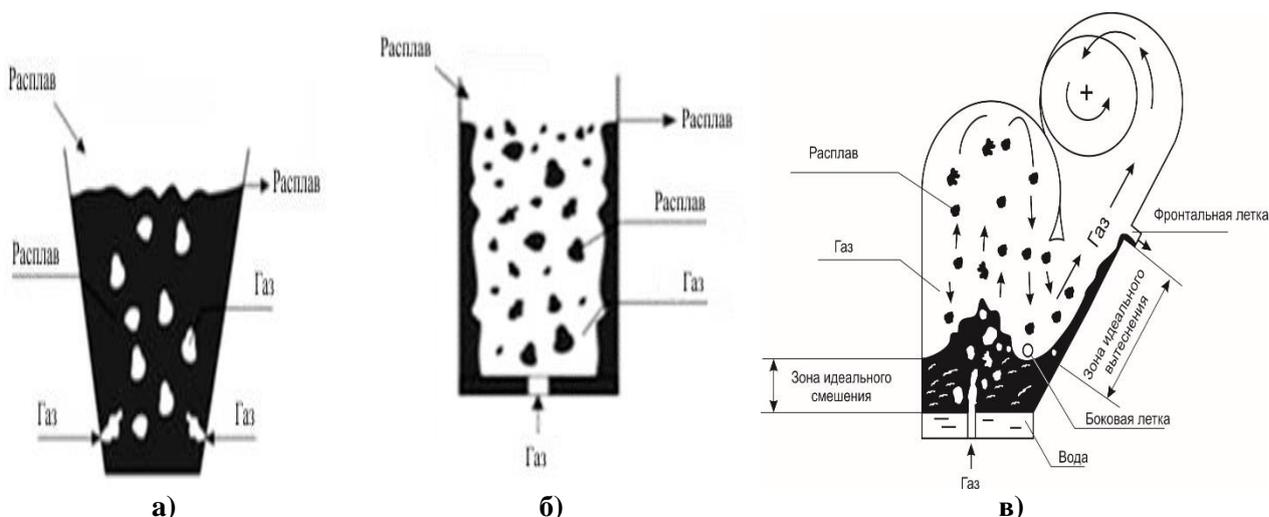


Рисунок 1 Способы обработки сырья в расплаве: а) барботажный слой, б) кипящий слой расплава, в) слой расплава с инверсией фаз



Рисунок 2 Общий вид пилотной установки

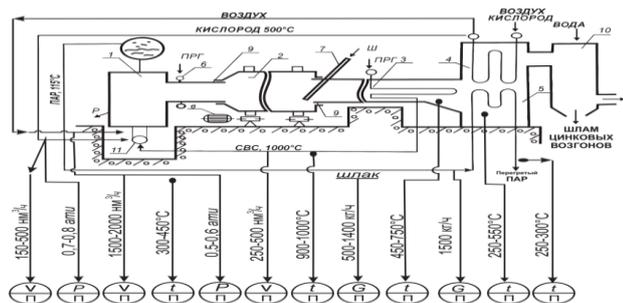


Рисунок 3 Схема измерений и материальных потоков пилотной установки

В таблицах 1 и 2 приведены результаты экспериментов. Условные обозначения в таблицах 1 и 2: $P_{ш}$ – производительность установки по шлаку, M_g – масса ванны расплава в реакторе, V_{O_2} – расход кислорода, $V_{прг}$ – расход природного газа, $W_{э}$ – расход электроэнергии, $G_{пар}$ – выработка пара, $Zn^{нач}, Zn^{кон}$ – начальное и конечное содержание цинка в шлаке, E – степень извлечения цинка, « v » – удельный расход природного газа на тонну цинка, I_c/G_b – отношение импульса газов в соплах продувочной

решетки к весу ванны расплава, $I_c = m_2 \cdot W_c$, где m_2 – массовый расход газа в соплах продувочной решетки, W_c – скорость газов в сопловой решетке, $G_b = M_g \cdot g$, где g – ускорение свободного падения.

Данные таблицы 1 демонстрируют, что степень восстановления цинка « E » растет, а удельный расход природного газа « v » уменьшается при смене способов обработки от барботажного слоя до слоя инверсии фаз.

Таблица 1 Сравнительные результаты экспериментов для барботажного слоя, кипящего слоя расплава и слоя расплава инверсии фаз при переработке «бедных» по цинку шлаков

Способы обработки расплава	$P_{ш}$, кг/ч	Мв, кг	I_c/G_b	V_{O_2} , $нм^3/ч$	$V_{прг}$, $нм^3/ч$	$Zn^{нач}$, %	$Zn^{кон}$, %	E , %	$W_{э}$, кВт·ч	$G_{пар}$, кг/ч	v , $\frac{нм^3 ПРГ}{т Zn}$
1 Барботажный слой расплава (выпуск расплава с вертикального кессона) $I_c/G_b \leq 0,09$	1300	670	0,064	103	288	4,3	3,01	30	235	~1500	17173
2 Кипящий слой расплава (выпуск расплава с вертикального кессона) $I_c/G_b = 0,09-0,19$	1336	400	0,099 -0,26	108	305-319	4,3	2,32	42	230	~1500	12640
3 Слой расплава инверсии фаз (выпуск расплава с наклонного к-на $I_c/G_b = 0,19-0,26$	1400	130	0,26	105	319	4,3	0,8	70	230	~1500	7272

Таблица 2 Результаты экспериментов для слоя расплава инверсии фаз при переработке «богатых» по цинку шлаков.

Способ обработки расплава		$P_{ш}$, кг/ч	M_b , кг	I_c/G_b	V_{O_2} , $\text{нм}^3/\text{ч}$	$V_{\text{ПРГ}}$, $\text{нм}^3/\text{ч}$	$Zn^{\text{нач}}$, %	$Zn^{\text{кон}}$, %	E , %	$W_{э}$, кВт·ч	$G_{\text{пар}}$, кг/ч	$\frac{v}{\text{нм}^3 \text{ПРГ}} \cdot \text{т Zn}$
1	Слой расплава инверсии фаз (выпуск расплава с наклонного кессона) $I_c/G_b = 0,19 - 0,42$	594	90	0,42	115	317	9,63	3,4	69	235	~1500	7925

Сравнение данных таблиц 1 и 2, для слоя инверсии фаз, по удельному расходу природного газа на переработку «бедных» по цинку отвальных шлаков ($Zn \leq 4/3\%$, $v = 7272 \frac{\text{нм}^3 \text{ПРГ}}{\text{т Zn}}$) и «богатых» шлаков ($Zn \geq 10\%$, $v = 7925 \frac{\text{нм}^3 \text{ПРГ}}{\text{т Zn}}$) показывает небольшую разницу ~8%.

Таким образом, полученные экспериментальные данные показывают, что в слое инверсии фаз удельный расход топлива на переработку «бедных» по цинку отвальных и «богатых» шлаков примерно одинаков.

Согласно технико-экономическим расчетам выполненным в Унипромеди [22], фьюмингование шлаков рентабельно при концентрации цинка свыше 5%. Если учесть, что при вельцевании «бедных» шлаков удельный расход топлива повысится в ~ 2 раза, то этот предел для отвальных шлаков будет еще выше. Опытные данные полученные способом слоя инверсии фаз противоречит такому утверждению и дает основание полагать, что на установке «реактор инверсии фаз-трубчатая печь» «бедные» по цинку отвальные шлаки могут перерабатываться наравне с «богатыми» с примерно одинаковым удельным расходом топлива.

Для поиска оптимальных режимов продувки были проведены серий экспериментов, результаты которых графически отображены на рисунке 4. Согласно рисунка 4, степень извлечения цинка E в слое инверсии фаз имеет экстремум при $I_c/G_b = 0,83$. В интервале $\frac{I_c}{G_b} = 0,83 - 1,0$ идет уменьшение степени возгонки цинка. При $\frac{I_c}{G_b} > 1,15$ происходит полное вытеснение слоя материала из реактора, что связано с превышением подъемных сил газа над гравитационной силой частиц шлака. Также определено зависимость массы ванны от производительности реактора. В отличие от барботажного и кипящего слоев, где масса ванны

M_b не зависит от производительности $P_{\text{риф}}$, в слое инверсии фаз M_b зависит от $P_{\text{риф}}$ по прямолинейному закону (рис.5).

Анализ результатов экспериментов

В процессе экспериментов на «бедных» по цинку шлаках, при выпуске расплава с вертикального кессона, в режиме кипящего слоя расплава с $I_c/G_b = 0,099$ и за пределами режима кипящего слоя расплава с $I_c/G_b = 0,26$, степень извлечения цинка не повысилась выше $E = 42\%$ (табл.1, п.2). Так как выпуск расплава с вертикального кессона в вышеуказанных диапазонах продувок определяется режимом идеального смешения, то из этого можно заключить, что возможности увеличения извлечения цинка в слое с идеальным смешением, только за счет повышения интенсивности продувки, имеет некоторый предел, обусловленный внутренними физико-химическими процессами.

После проведения экспериментов с выпуском расплава с наклонной части реактора, (условно назовем режимом идеального вытеснения), при том же значении $I_c/G_b = 0,26$, было достигнуто удовлетворительное значение степени возгонки цинка - $E = 70\%$ (табл.1, п.3). Таким образом, перед экспериментатором встает естественный вопрос, какие физико-химические процессы повлияли на такой результат?

Инструментом для объяснения результатов опытов может служить характер изменения энергии Гиббса в термодинамической системе восстановления цинка из его оксидов.

Цинк в отвальных шлаках находится в форме сложных соединений, как силикат цинка (Zn_2SiO_4), феррит цинка ($ZnFe_2O_4$) и т.п. Прежде чем восстановить цинк из таких сложных соединений, потребуется их разложение на простые молекулы (см. табл. 3 пункты 1 и 2) и только затем возгонка цинка в газовую фазу (см. табл. 3 пункт 3).

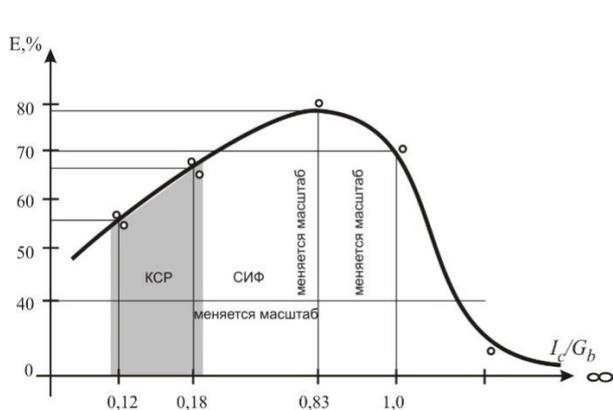


Рисунок 4 Зависимость степени извлечения цинка от способа продувки «бедного» шлака при производительности реактора $P_{\text{ш}} \sim 1300$ кг/ч. КСР – кипящий слой расплава, СИФ – слой инверсии фаз

Как следует из таблицы 3, характер изменения энергии Гиббса для образования сложных молекул Zn_2SiO_4 и $ZnFe_2O_4$ из простых молекул - ZnO , SiO_2 , Fe_2O_3 отрицательный, а характер изменения энергии Гиббса для реакций распада силиката (Zn_2SiO_4) и феррита цинка ($ZnFe_2O_4$) на эти простые компоненты (ZnO , SiO_2 , Fe_2O_3) положительный. Среднее значение константы равновесия (K) реакций образования сложных молекул из простых компонентов (табл.3, п.4,5), на два порядка (~ 100 раз), больше чем у реакции распада сложных молекул на простые (табл.3, п.1,2). Поэтому, с большей вероятностью можно ожидать, что в режиме «идеального» смешения, в слое расплава идет два противоположных по направлению реакций: (а) – реакции разложения сложных молекул на простые компоненты и (б) – реакции образования сложных молекул из простых компонентов. Из последнего можно констатировать, что в упомянутых выше режимах «идеального» смешения (0,099-0,26), с выпуском расплава с вертикального кессона, из-за перегруппировки между рекомбинированными молекулами ZnO , SiO_2 , Fe_2O_3 с вновь образованием силикатов и ферритов цинка (Zn_2SiO_4 , $ZnFe_2O_4$), рост извлечения цинка не наблюдалось.

Способ выпуска расплава с наклонной части реакторанами был условно назван режимом «идеального» вытеснения. Так как в наклонном слое расплава «идеального» вытеснения (см. рис. 6), также идет процесс разложения сложных молекул и каждая элементарная струйка в нем движется

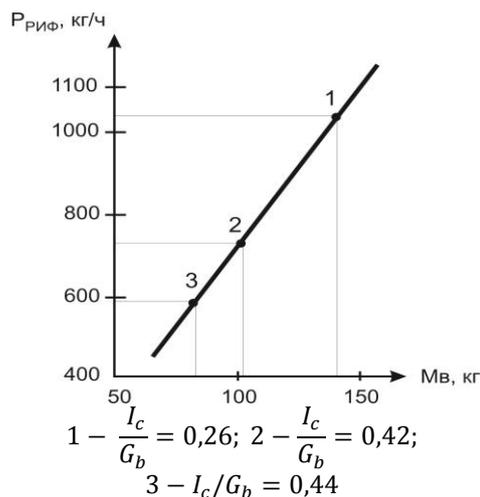


Рисунок 5 Зависимость массы ванны от производительности по шлаку в СИФ

параллельно друг другу, то вероятность смешения рекомбинированных компонентов - ZnO , SiO_2 , Fe_2O_3 , соответственно, вновь образования из них сложных молекул - Zn_2SiO_4 , $ZnFe_2O_4$ уменьшается и степень восстановления цинка по формуле $ZnO + CO = Zn^{\Gamma} + CO_2$ возрастает.

Вышесказанное также относится к восстановлению железа из шлаков (табл.3, п. 6-9). В [21] приведены результаты опытов по восстановлению железа из отвальных шлаков.

После проведения каждого эксперимента измерялась толщина гарниссажного слоя огневой поверхности кессонов плавильного реактора (рис.7). Средняя толщина гарниссажного слоя вертикальных, потолочных и наклонных кессонов с выпуском расплава с вертикального кессона составила $\delta = 3-5$ мм. При выпуске расплава с наклонного кессона, средняя толщина гарниссажного слоя вертикальных и потолочных кессонов оставался $\delta = 3-5$ мм, а толщина гарниссажного слоя наклонного кессона, на участке взаимодействия падающего газокapельного потока и вытесняемого расплава (рис.6), выросла до 30 – 35 мм. На наш взгляд, утолщение гарниссажного слоя на наклонной части реактора дополнительно указывает на восстановление цинка с протеканием реакции с эндотермическим эффектом – $ZnO + CO = Zn^{\Gamma} + CO_2 - Q_{\text{энд}}$. Последняя реакция, вероятно, повлияла на «замораживание» подслоя, в районе взаимодействия падающего газокapельного потока и слоя расплава, движущегося в направлении к летке.

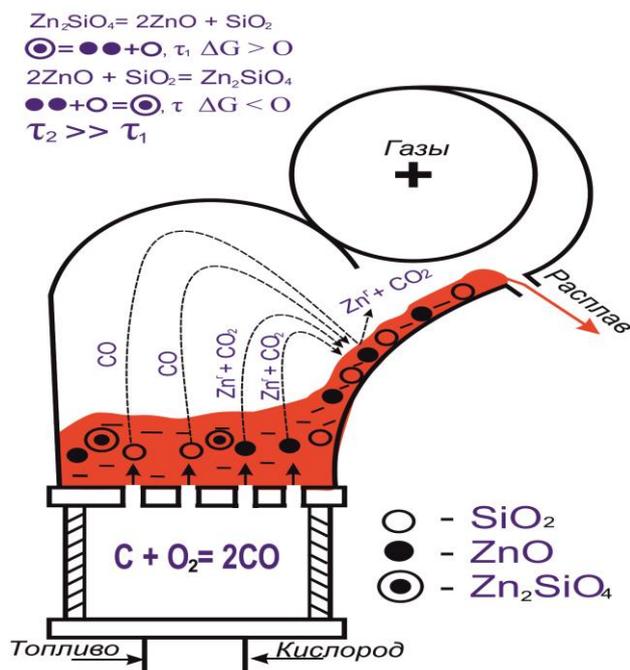


Рисунок 6 Схема восстановления цинка в реакторе с вытеснением расплава с наклонного кессона

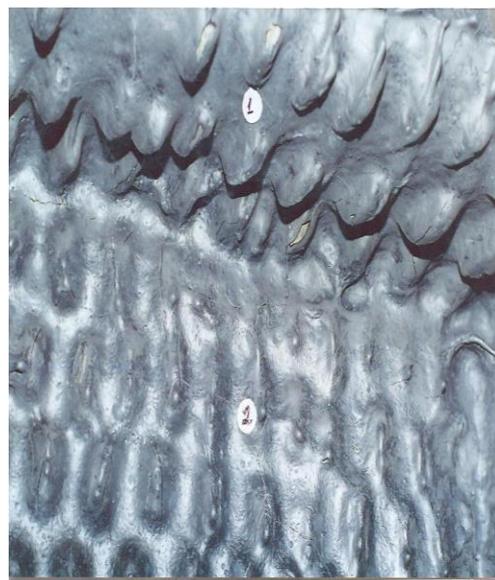


Рисунок 7 Гарниссажный слой шлаков на ошпикованной поверхности кессонов испарительного охлаждения реактора при $t=1400^{\circ}C$. 1- потолочный кессон, 2 – боковой кессон. Удельная плотность теплового потока $q=135-145$ кВт/м²

Таблица 3 Термодинамические характеристики реакций при $t=1400^{\circ}C$, [23]

№	Реакций	ΔG , кДж	K
1	$Zn_2SiO_4 = 2ZnO + SiO_2$	35.73	0.077
2	$ZnFe_2O_4 = ZnO + Fe_2O_3$	32.37	0.097
3	$ZnO + CO = Zn + CO_2$	-9.5	1.977
4	$2ZnO + SiO_2 = Zn_2SiO_4$	-35.73	13.062
5	$ZnO + Fe_2O_3 = ZnFe_2O_4$	-32.37	10.256
6	$FeSiO_3 = FeO + SiO_2$	6,763	6,149E-001
7	$FeO + SiO_2 = FeSiO_3$	-6,763	1,626E+000
8	$FeAl_2O_4 = FeO + Al_2O_3$	36,520	7,241E-002
9	$FeO + Al_2O_3 = FeAl_2O_4$	-36,520	1,381E+001

Сравнение потребления топлива агрегатом «РИФ-ТП» сосуществующей вельц-печью

- вельц печь Лениногорского полиметаллического комбината, перерабатывающая холодный шлак: $L \times D = 70M \times 5M$, технологический объем печи 816м³, среднесуточная производительность по шлаку 750т. Среднечасовая производительность 31,25т. Расход коксика ~ 480 кг/т шл, мазута ~33 кг/т шл. $Zn^{нач}=10\%$, $Zn^{кон}=2\%$, $E=80\%$. Удельная производительность $p_v^{вельц}=3,82$ кгZn/м³·ч, удельный расход коксика $v_{кокс}=6000$ кг/т Zn (6000 кгу.т./тZn).

Приведенный удельный расход условного топлива в действующей системе вельцевания «богатого» шлака производительностью 31,25т/ч:

$$\begin{aligned}
 v_{пр}^{вельц} &= v_{кокс} + v_{мазут} + v_{т.д.} \\
 &= \frac{B_{кокс} + B_{мазут} + B_{т.д.}^{\text{э}}}{P_{Zn}} = \\
 &= \frac{15000 + 1400 + 303}{2,52} = 6628 \frac{\text{кгу.т.}}{\text{тZn}}
 \end{aligned}$$

Здесь $B_{т.д.}^{\text{э}}$ – расход условного топлива на производство электроэнергии затраченной на привод тяго-дутьевой установки вельц-печи.

Приведенный удельный расход условного топлива на пилотную установку «реактор инверсии фаз-трубчатая печь» для переработки «бедного» шлака производительностью ~1,4 т/ч (данные рассчитаны на основе табл.1):

$$\frac{B_{\text{пр}} + B_{\text{ГД}} + B_{\text{O}_2} - B_{\text{пар}}}{P_{\text{Zn}}} = \frac{367 + 40 + 8,5 - 138}{0,04214} = 6585 \frac{\text{кг.У.Т.}}{\text{м.Зн}}$$

Соотношение приведенных удельных расходов топлива вельц-печи и пилотной установки:

$$\frac{\epsilon_{\text{пр}}^{\text{вельц}}}{\epsilon_{\text{пр}}^{\text{пу}}} = \frac{6628}{6585} = 1,007 \quad (1)$$

Согласно формуле (1) приведенный удельный расход условного топлива (*пурут*) в пилотной установке «реактор инверсии фаз-трубчатая печь» при переработке «бедных» шлаков примерно одинаков с «пурут» действующей вельцпечи обрабатывающей «богатые» шлаки.

Прогноз теплотехнических характеристики к промышленной установки «реактор инверсии фаз-трубчатая печь». Методом аффинного моделирования описанной в [16] выполнен расчет теплотехнических характеристик промышленного образца реактора инверсии фаз, результаты которых представлены в графическом виде на рисунке 8. Показанная на рис.8 удельный расход условного топлива в прогнозируемом промышленном образце установки «реактор инверсии фаз-трубчатая печь» производительностью 30 т/ч, перерабатывающей «бедный» шлак (~3500 $\frac{\text{кг.У.Т.}}{\text{м.Зн}}$) будет в 1,5 - 1,7 раза ниже чем в вельц-печи производительностью 30 т/ч перерабатывающая «богатый» шлак (6000 $\frac{\text{кг.У.Т.}}{\text{м.Зн}}$). Согласно [24] расчетная удельная производительность агрегата «реактор инверсии фаз-трубчатая печь» производительностью 30 т/ч по «бедному» шлаку $p_v^{\text{риф-тп}} = 2,58 \text{ кг.Зн/м}^3 \cdot \text{ч}$. Тогда соотношение удельных производительностей $\frac{p_v^{\text{вельц}}}{p_v^{\text{риф-тп}}} = \frac{3,82}{2,58} = 1,48$

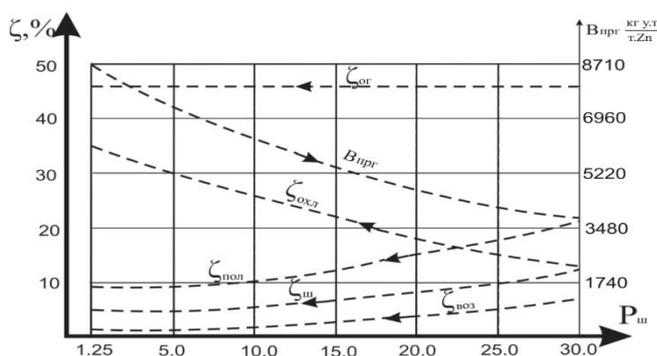


Рисунок 8 Зависимость теплотехнических характеристик прогнозируемого реактора инверсии фаз от производительности по шлаку. $\zeta_{\text{ог}}$ – доля теплоты отходящих газов в тепловом балансе реактора, $\zeta_{\text{охл}}$ – доля теплоты охлаждающей кессоны водой, $\zeta_{\text{пол}}$ – доля полезно использованной теплоты, $\zeta_{\text{ш}}$ – доля теплоты шлакового расплава, $\zeta_{\text{воз}}$ – доля теплоты возгонов цинка, $B_{\text{пр}}$ – расход природного газа в условном топливе, $P_{\text{ш}}$ – производительность реактора по шлаку.

Таким образом, в случае внедрения агрегата «реактор инверсии фаз-трубчатая печь» для переработки «бедных» шлаков, по сравнению с вельц-печью перерабатывающей «богатый» шлак, удельный расход условного топлива сократится в 1,5-1,7 раза, а удельная производительность вырастет в 1,4-1,5 раза. Промышленная реализация агрегата «реактор инверсии фаз-трубчатая печь» позволила бы рентабельно перерабатывать отвалы шлаков Шымкентского свинцового завода, клинкер вельцевания, «бедные» цинковые руды комбината «Ачполи-металл», хвосты обогащения Текелийского

горно-металлургического комбината и других объектов цветной металлургии.

Выводы

1. В период проведения экспериментов в режиме «плавка-восстановление» было переработано ~250т «бедного» шлака. Установка проработала безаварийно около 1000 часов, что подтверждает надежность его конструкции.

2. Результаты экспериментов для барботажного слоя, кипящего слоя расплава и

слоя расплава инверсии фаз при переработке «бедных» по цинку шлаков показывают, что степень возгонки цинка растёт, а удельный расход природного газа уменьшается при смене способов обработки от барботажного слоя до слоя инверсии фаз.

3. Полученные в пилотной установке экспериментальные данные показывают, что в слое инверсии фаз удельный расход топлива на переработку «бедных» по цинку отвальных и «богатых» шлаков примерно одинаков. Последнее положение противоречит устоявшемуся мнению металлургов, что переработка шлаков с концентрацией цинка менее 5% нерентабельна.

4. Анализ реакций восстановления цинка на основе характера изменения энергии Гиббса реакций позволяет дать определение слою инверсии фаз как комбинацию режимов «идеального» смешения и «идеального» вытеснения.

5. Приведенный удельный расход

условного топлива (*нурут*) в пилотной установке «реактор инверсии фаз-трубчатая печь» при переработке «бедных» шлаков примерно одинаков с «нурут» действующей вельц-печи обрабатывающей «богатые» шлаки.

6. Результаты расчетов демонстрируют, в случае внедрения промышленного образца агрегата «реактор инверсии фаз-трубчатая печь» для переработки «бедных» шлаков, по сравнению с вельц-печью перерабатывающей «богатый» шлак, удельный расход условного топлива сократится в 1,5-1,7 раза, а удельная производительность вырастет в 1,4-1,5 раза.

7. Промышленная реализация агрегата «реактор инверсии фаз-трубчатая печь» позволила бы рентабельно перерабатывать отвалы шлаков Шымкентского свинцового завода, клинкера вельцевания, «бедные» цинковые руды комбината «Ачполиметалл», хвосты обогащения Текелийского горно-металлургического комбината и других объектов цветной металлургии.

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Өнеркәсіптік қалдықтарды өңдеудің энергия үнемдейтін әдісін жасау

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Түйіндеме. Техногендік қалдықтарды қайта өңдеудің энергия үнемдейтін тәсілі – инверсиялы фаза балқыма қабатының "мінсіз" араластыру және "мінсіз" ығыстыру режимдерінің комбинациясы ретінде әзірленді. Оның негізінде жаңа буын балқыту агрегаты-"инверсиялы фаза реакторы-құбырлы пеш" құрылды. Тәжірибеден алынған деректер инверсиялы фаза қабатында мырышы "кедей" және мырышы "бай" шлактарды өңдеуге арналған отынның меншікті шығыны шамамен бір екенін көрсетеді. Соңғы жағдай мырыш концентрациясы 5% - тен кем шлактарды өңдеу тиімсіз деген металлургтердің тұрақтаған пікіріне қайшы келеді. Есептеу бойынша, "кедей"шлактарды өңдеуге арналған "инверсиясылы фаза реакторы-құбырлы пеш" агрегатының өнеркәсіптік үлгісін енгізген жағдайда, "бай" шлақты қайта өңдейтін вельц-пешпен салыстырғанда шартты отынның меншікті шығыны 1,5-1,7 есе қысқарады, ал меншікті өнімділік 1,4-1,5 есе өседі. "Инверсиясылы фаза реакторы-құбырлы пеш" агрегатын өнеркәсіпке енгізгенде фьюмингтеу шлактарының үйінділерін, вельцпеш клинкерін, "кедей" мырыш кендерін, байыту қалдықтарын және түсті металлургияның басқа да тастандыларын тиімді өңдеуге мүмкіндік берер еді.

Түйін сөздер: энергияны үнемдеу әдісі, фазалық инверсиялық реактор - түтік пештері, «мырышсыз» шлактар, «идеалды» араластыру және жылжыту режимдерінің үйлесімі.

Development of energy-efficient method for processing industrial waste

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Abstract. An energy-saving method for processing technogenic waste has been developed — a smelt layer with inversion phase as a combination of “ideal” mixing and “ideal” displacement regimes. On its basis, a new generation of melting unit was created - the “reactor inversion phase - rotary kiln”. Experimental data show that in the inversion phase layer the specific fuel consumption for processing the “poor” on zinc and “rich” on zinc slags is approximately the same. The latter provision contradicts the prevailing opinion of metallurgists that the processing of slag with a zinc concentration of less

than 5% is unprofitable. Calculation results demonstrate that in case of implementation of an industrial sample of “reactor inversion phase - rotary kiln for processing “poor” slag, compared to the Waelz kiln processing “rich” slag, the specific consumption of fuel will be reduced by 1.5-1.7 times and specific productivity will increase 1.4-1.5 times. The industrial realization of “reactor inversion phase -rotary kiln” would allow cost-effective processing of fuming slag dumps, Waelz clinker, “poor” zinc ores, enrichment tails and other non-ferrous metal wastes.

Key words: energy-saving method, phase inversion reactor — tube furnace, “zinc-poor” slags, a combination of “ideal” mixing and displacement modes.

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