***S.V.Gorbatko MATERIALS FOR RESTORATION REFRACTORY MASONRY THERMAL AGGREGATES***

*The problem about resistance of the brickwork for coke-oven batteries arises during their exploitation. Hence, maximal enlargement of its operation life is of present interest. Successful solution of this problem defines the main technical and economic parameters of the whole heat unit.*

*One of the ways of repairs is the method of the brickwork revitalizing according the technology of self-propagating high-temperature interaction (SHI).*

*For the first time this method was applied for the synthesis of infusible inorganic compounds. SHI method is the combustion action of any chemical nature, which leads to the formation of the valuable solid materials for practical use. The environment, which is capable of reacting in the SHI regime, can be different: solid, gaseous, mixed. The only importance is that the chilled product of combustion should be in solid state with valuable service property.*

*The remarkable characteristics for such processes are the next: combustible components are metals and oxidizing agents are nonmetals. The temperature of the process can vary in very wide range from 1100-1400°K to 3000-3650°K. After initiation the process does not have chaotic fire type, but has directed wave nature.*

*The possibility of application of mentioned method and mixtures is urgent for repairs of blast-furnace brickwork. They will allow solving quite a number of problems connected to enlargement of the operation life for working area of coking chamber.*

***Key words:** coking chamber, brickwork, siliceous refractory material, destruction, revitalizing.*

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# INTENSIFICATION OF GRAVITATIONAL METHOD OF AMMONIAC WATERS PURIFICATION FROM COAL TAR IMPURITIES

*Ammoniac waters of coke-chemical production, including ammonia-tar liquor and condensate of primary gas coolers (PGC), are made up more than 50% of total effluent of catching chemical products department. Ammoniac waters contain impurities of aromatic tars and oils (coal tar substances) in the number of 300-2200 mg/l. The presence of tars and oils in ammoniac waters complicates their further processing, reduces the effectiveness of technological processes, contaminates equipment with tar deposits.*

*The gravitational method can not provide effective purification of ammoniac waters from fine disperse tar particles which radius is smaller than 20 microns. Therefore, for enlargement of tar phase particles the coalescence was suggested.*

*In earlier works it was proved that mineral fiber material of diabase group (MFD) leads to increased sizes of disperse particles of coal tars and oils, and redistribution of the fraction in the direction of larger particles. The effect of coalescence is 75-78% depending on the temperature, flow rate, packing density of mineral fiber material.*

*It is shown that preliminary processing of ammoniac water by passing it through a coalescing filter intensifies the gravitational settling of coal tar impurities in the settling tanks.*

*Based on theoretical and experimental studies it is suggested to include a coalescing filter on coke-chemical plants technological scheme of ammoniac water purification from coal tar impurities. In the present technological scheme the process of coalescence is auxiliary. However, due to a coalescing filter high efficiency of ammoniac water purification can be provided. Coalescence method can be attributed as a regenerative method, as during the processes tar water emulsion is separated into two phases, one of which is tar. Recycling of tar can be an additional economic achievement in implementation of this method.*

***Keywords**: ammoniac water; coal tar water emulsions; mineral fiber material; coalescing filter; gravitational settling; technological scheme; purification.*

Ammoniac waters of coke-chemical production, including ammonia-tar liquor and condensate of primary gas coolers (PGC), are made up more than 50% of total effluent of catching chemical products department. These waters are formed from the moisture of coal mixture and the so-called pyrogenetic moisture. Ammoniac waters contain impurities of aromatic tars and oils (coal tar substances) in the number of 300-2200 mg/l. These waters are low concentrated polydisperse emulsions (coal tar water emulsions) of direct O/W type (amount of tars and oils 0.01 - 0.2%) with high dispersity of tar phase [1-4].

The presence of tars and oils in ammoniac waters complicates their further processing, reduces the effectiveness of technological processes, contaminates equipment with tar deposits. Tars and oils from ammoniac water then flow to biochemical plant and have a negative influence on process of their purification by means of microorganisms.

By dispersion degree the emulsions are divided into fine-dispersed with droplet size of 0,2 - 20 microns, the average dispersed - 20 to 50 microns and coarsely dispersed - more than 50 microns.

The gravitational method of ammoniac waters purification from coarse particles is widespread in the coke-chemical plants due to its simplicity. The main point of this method lies in sedimentation of particles of impurities by gravity. The sedimentation rate of disperse phase particles is dependent on the particle size, the density difference between the disperse phase and the disperse medium, and the viscosity of aqueous phase.

To separate the tar substances from ammoniac water vertical settling tanks of continuous sedimentation are used. Vertical settling tanks are cylindrical in shape (height 5- 8 m and diameter 5-6 m). Movement of brightening water in the tanks is in the vertical direction - from the bottom upwards. Suspended particles are deposited in the upstream. The calculated speed of the upstream usually is 0.2 - 0.5 mm / sec. The height of sedimentation zone is typically 4-5 m. Conditional stay of ammoniac water in the sedimentation zone varies from 2 to 5 hours. Technological scheme of ammoniac water purification includes three vertical settling tanks, 265 $m^3$ each at a water flow rate 20 to 30 $m^3$ / h.

The efficiency of vertical tanks is largely determined by coarseness of the deposited particles. Their sedimentation rate depends mainly on the size of particles, as the difference between densities of aqueous and tar phases is small and amounts 141-160 kg/$m^3$. Table 1 shows the calculated data of sedimentation rate of tar phase particles of different diameter in ammoniac water while motionless.

**Table 1.** Sedimentation rate of spherical tar particles in ammoniac water

| Radius of particles, micron | Sedimentation rate, mm/sec | Time for sedimentation on 10 cm, min |
|---|---|---|
| 10 | 0,05 | 33 |
| 20 | 0,2 | 8,2 |
| 30 | 0,45 | 3,7 |
| 40 | 0,8 | 2,1 |
| 50 | 1,3 | 1,3 |
| 100 | 5,0 | 0,33 |

As the particles of tars and oils accumulate in upward current while mainstream moves at a rate of 0.2 - 0.5 mm/sec, it is obvious that this sedimentation is possible only when the rate of disperse particles is greater than the mainstream rate of ammoniac water.

The presented data in Table 1 show that in vertical settling tanks ammoniac water can be purified of tar particles with radius larger than 30 microns.

Investigation of fractional composition of ammoniac water tar phase (condensate of PGC) before and after the settling tanks in one of coke-chemical plants (Table 2) showed that in settling tanks are deposited mainly particles with a radius of more than 20 microns.

It is necessary to note that the content of fraction 0-20 microns in the condensate of PGC before purification is larger than in ammoniac water after purification. This can be explained by the fact that sedimentation of polydisperse tar particles accompanied by their agglomeration and the gradual enlargement. The main reason for agglomeration is the gravitational or kinetic coagulation - the collision and coalescence of particles by different rate of sedimentation of particles of different size. Thus, some of the particles with a radius of less than 20 micron is enlarged to a size of more than 20 micron and separated from the aqueous phase. However, in purified ammoniac water the content of tar particle with radius of less than 20 micron is 70 - 81%.

**Table 2.** Fractional composition of ammoniac water tar phase before and after settling tanks

| Fraction, micron | Condensate of PGC, sample 1 | | | Condensate of PGC, sample 2 | | |
|---|---|---|---|---|---|---|
| | Before settling tanks, mg/l | After settling tanks | | Before settling tanks, mg/l | After settling tanks | |
| | | mg/l | % | | mg/l | % |
| 0-20 | 148 | 122 | 81 | 132 | 101 | 70 |
| ›20 | 1094 | 28 | 19 | 1895 | 33 | 30 |
| Total | 1242 | 150 | 100 | 2027 | 134 | 100 |

Based on written above it can be concluded that the residual tar particles content in ammoniac water after gravitational purification is determined by concentration of particles less than 20 microns.

Ammoniac waters of coal high temperature pyrolysis, which are coal tar water emulsions, have high dispersion and aggregative stability. Containing of tar particles with a radius of less than 20 microns is 130 - 600 mg/l [1-3].

As shown above, the gravitational method cannot provide effective purification of ammoniac waters from fine disperse tar particle which radius is smaller than 20 microns. Therefore, for enlargement of tar phase particles the coalescence was suggested [3-4].

Coalescence is aggregation of emulsion disperse particles with complete elimination of initially separating surface. This changes the phase-disperse state and leads to enlargement of tars and oils droplets in base emulsion. The system becomes kinetically unstable and quickly segregates.

To change the phase-disperse state of tar water emulsions the coalescence of particles of tars and oils by ammoniac water filtration through a layer of mineral fiber was studied [3-4]. The purpose of infiltrating charging in coalescing filter - enlargement of small emulsified tar droplets, unlike commonplace filters act as holding environment.

The coalescence of coal tars and oils on mineral fiber proceeds as follows. Particles of tars and oils contact with fiber surface and by adhesive interaction form a film on it. Holding the particles depends on particles size, their velocity, and on stability of tar water emulsion. Gradually, the film thickness increases, the narrow channels between the fibers are filled with tar substances that bind a load into the single hydraulic system. A major influence on thickness of the resulting film has tar substances viscosity and velocity of liquor in the space between fibers. During filtration on this stage the so-called filter charging is completed. When filtering from the top downward the film flow of tar substances comes off the fiber of coalescing material in the form of drops, which are carried by water flow.

Thus, the efficiency of coalescing filter is determined by the overall effect of the molecular-surface and hydrodynamic forces, which depend on the physical and chemical properties of tar water emulsion and mineral fiber, and a liquid flow rate.

In [3-4] shown that the mineral fiber material of diabase group (MFD) provides enlargement of disperse particles of coal tars and oils, and redistribution of the fraction in the direction of larger particles. The effect of coalescence is 75-78% depending on the temperature, flow rate, packing density of mineral fiber material.

In the pilot plant, consisting of coalescing filter and settling tank, a series of experiments concerning coalescence effect of tar particles on the efficiency of gravitational lightening of ammoniac water while motionless. Figure 1 shows the kinetic curves of tars and oils sedimentation while motionless for condensate of PGC before and after filtration through a layer of mineral fiber material of diabase group.

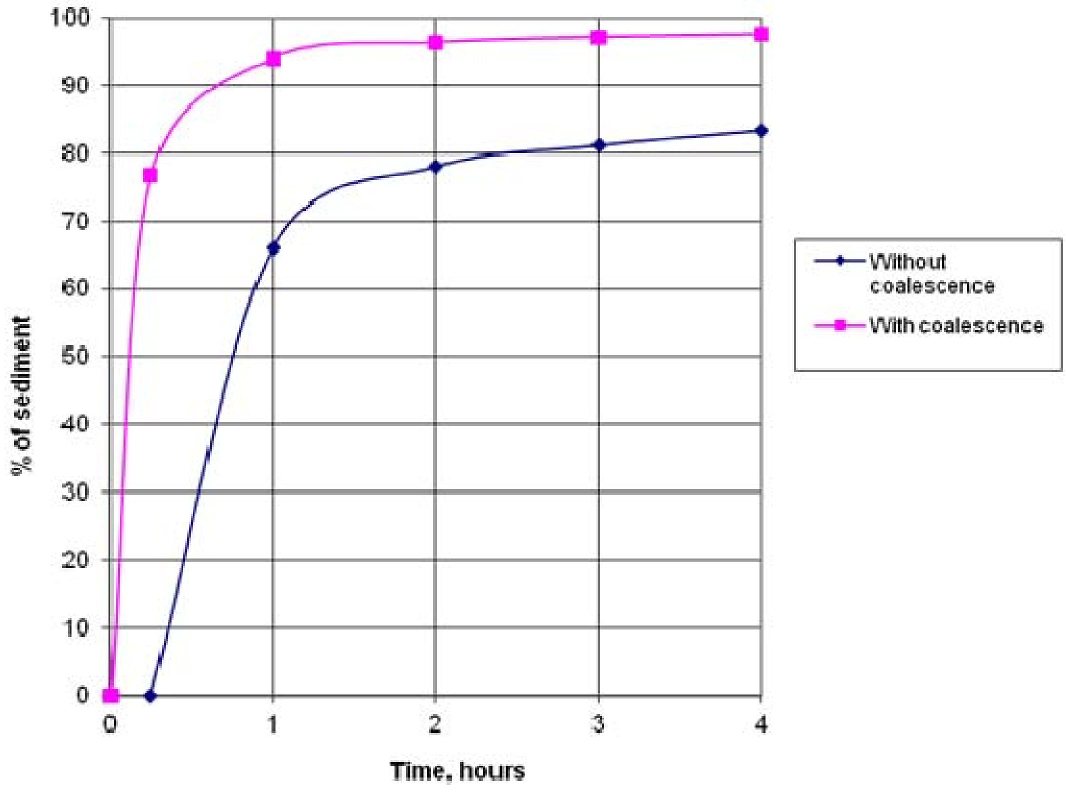


**Fig. 1**. Kinetic curves of tar particles sedimentation in ammoniac water while motionless

Kinetic curves of sedimentation clearly demonstrate the advantage of preliminary stage of water treatment - the coalescence, after which the efficiency of water purification increases by 18-25%, and is 95-98% depending on the time of settling. This effect is observed as a result of enlargement of tar particles on coalescing material (the coalescence effect is 76.7%, the content of particles with radius> 30 microns - 70%) and to increase of their sedimentation rate.

In the diagram (Fig. 2) it is shown that the concentration of impurities of tar substances in purified water, passed through the stage of coalescence is much less than while settlement the base ammoniac water. During ammoniac water settlement (after coalescence) for 1, 2, 3 hours tar particles concentration in the clarified water is 5-7 times lower than in water without pre-treatment, and is respectively 34, 22 and 18 mg / l.

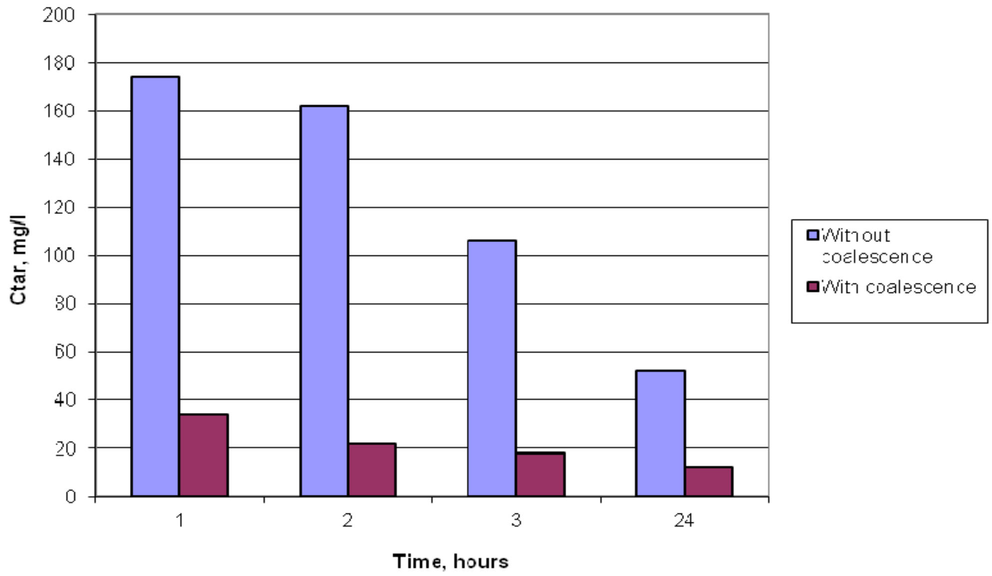


**Fig. 2**. The residual tar particles content in purified ammoniac water after settlement

Pre-treatment of ammoniac water by passing it through a coalescing filter intensifies the gravitational settling of impurities in the settling tanks.

Based on theoretical and experimental studies it is suggested to include a coalescing filter into existing on coke-chemical plants technological scheme of ammoniac water purification from coal tar impurities (Fig. 3).

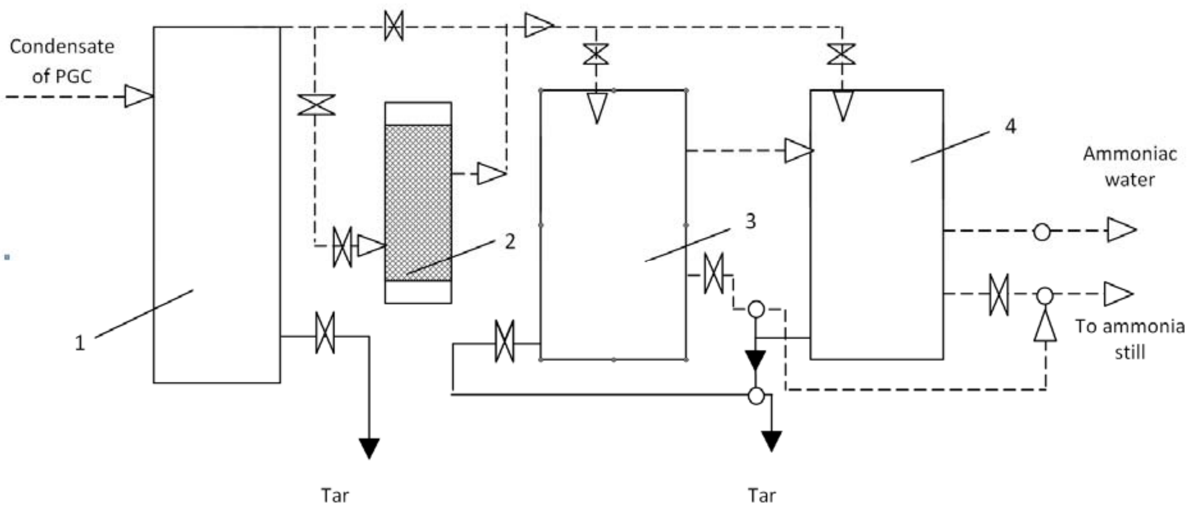


**Fig. 3**. Technological scheme of ammoniac water purification

The scheme includes three vertical settling tanks 1,3,4 and coalescing filter 2. In the first settling tank the separation of coarse emulsion particles and impurities takes place. Removal of solids before coalescing filter is necessary to prevent its clogging. After separation of solids ammoniac water flows by gravity to a coalescing filter 2, which is filled with mineral fiber material. Fluid movement is from the bottom upwards. Upstream allows to prevent undesirable compaction of load and increasing the hydraulic pressure of filter.

At steady state operation of coalescing filter 2 on the fiber surface, a layer of the disperse phase is formed, and subsequent coalescence of tars and oils droplets flows in the interaction with this layer. Aggregative tar particles are removed from the filter with water flow and are separated in settling tanks 3 and 4. Purified from tar particles ammoniac water comes to processing in an ammonia still.

In the presented technological scheme the process of coalescence is subsidiary. However, due to a coalescing filter high efficiency of ammoniac water purification can be provided. Coalescence method can be attributed to the regenerative method, as during the processes tar water emulsion is separated into two phases, one of which is tar. Recycling of tar can be an additional economic boost for implementation of this method.

Coalescence method is one of the most promising methods for ammoniac water purification from impurities of aromatic tars and oils. In combination with settling tanks the coalescing filter with mineral fiber MFD intensifies the ammoniac water purification by gravitational method.

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***И.Г. Крутько, Ю.В. Пульникова ИНТЕНСИФИКАЦИЯ ГРАВИТАЦИОННОГО МЕТОДА ОЧИСТКИ АММИАЧНЫХ ВОД ОТ СМОЛИСТЫХ ПРИМЕСЕЙ***

*Показано, что предварительная подготовка аммиачной воды путем пропускания ее через коалесцирующий фильтр интенсифицирует процесс гравитационного осаждения примесей смолистых веществ в отстойниках.*

*На основании теоретических и экспериментальных исследований предложено включить в существующую на коксохимических заводах технологическую схему очистки аммиачной воды от смолистых веществ коалесцирующий фильтр.*

***Ключевые слова:*** *каменноугольные водосмоляные эмульсии, аммиачные воды, минеральный волокнистый материал, коалесцирующий фильтр, гравитационное осаждение, технологическая схема, очистка*

***І.Г. Крутько, Ю.В. Пульникова ІНТЕНСИФІКАЦІЯ ГРАВІТАЦІЙНОГО МЕТОДУ ОЧИЩЕННЯ АМІАЧНИХ ВОД ВІД СМОЛИСТИХ ДОМІШОК***

*Показано, що передчасна підготовка аміачної води шляхом пропускання її через коалесцуючий фільтр інтенсифікує процес гравітаційного осідання домішок смолистих речовин у відстійниках.*

*На основі теоретичних та експериментальних досліджень запропоновано включити в існуючу на коксохімічних заводах технологічну схему очищення аміачної води від смолистих речовин коалесцуючий фільтр.*

***Ключові слова:*** *кам'яновугільні водосмоляні емульсії, аміачні води, мінеральний волокнистий матеріал, коалесцуючий фільтр, гравітаційне осідання, технологічна схема, очищення.*

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## К ВОПРОСУ О МЕХАНИЗМЕ ВЫДЕЛЕНИЯ ГИДРОКСИДА АЛЮМИНИЯ ИЗ РАСТВОРОВ АЛЮМИНАТА НАТРИЯ

*Предложена принципиально новая схема процесса карбонизации алюминатных растворов, включающая образование в качестве первичного продукта алюмокарбоната натрия и последующее его превращение в гидроксид алюминия в реакции с алюминатом натрия. Составлена математическая модель процесса, объясняющая причины загрязнения гидроксида алюминия соединениями натрия.*

***Ключевые слова:*** *алюминат натрия, гидроалюмокарбонат, карбонизация, математическая модель*

Карбонизация — один из методов, применяемых в практике производства глинозема для разложения алюминатных растворов с целью выделения кристаллической гидроокиси алюминия [1].

При получении глинозема способом спекания с известняком в спеках образуются соединения $12CaO{\cdot}7Al_2O_3$ и $CaO{\cdot}Al_2O_3$. Выщелачивание спеков содовым раствором приводит к разложению алюмокальциевых спеков с переходом глинозема в жидкую фазу в виде алюмината натрия ($NaAlO_2$) в соответствии с уравнениями [1, 2]:

$$12CaO{\cdot}7Al_2O_3 + 12\ Na_2CO_3 + 5\ H_2O \rightarrow 14\ NaAlO_2 + 12\ CaCO_3 + 10\ NaOH,$$

$$CaO{\cdot}Al_2O_3 + Na_2CO_3 \rightarrow 2\ NaAlO_2 + CaCO_3$$

Для выделения $Al(OH)_3$ целесообразно применение карбонизации, так как, наряду с гидроокисью алюминия, получается раствор соды, который используется как оборотный раствор. С химической точки зрения процесс карбонизации протекает в несколько стадий [3]. Диоксид углерода сначала расходуется на преодоление буферной емкости с последующим формированием рентгеноаморфной фазы, которая растворяется в избытке каустической щелочи:

$$CO_2 + 2\ OH^- = CO_3^{\ 2-} + H_2O; \quad (1)$$

$$CO_2 + 3\ H_2O = 2\ H_3O^+ + CO_3^{\ 2-}; \quad (2)$$

$$[Al(OH)_4]^- + H_3O^+ = AlOOH + 3\ H_2O; \quad (3)$$

$$AlOOH + OH^- + H_2O = [Al(OH)_4]^- \quad (4)$$