

## ELABORATION OF APPLICATION METHODS FOR TRICE OIL EMULSIONS AND OIL-SLIMES

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### Abstract

In this article the research in elaboration of non-waste reprocessing technology for oil emulsions, regenerating from oil-slime of Krasnodar oil-reprocessing plant is specified. According to the results of the research some technological solutions for the raw meal preparation for the production of bricks and haydite have been set forward. For the production of bricks and haydite we have used oil-slime, collected during the treatment of sewage and process waste water, which is a thick liquid of density 0.86 – 0.97 g/cm<sup>3</sup> (№ 2 and 3 in Chart 1), containing water, mechanical impurities and combustible fractions. Combustible fractions mainly consist of asphaltenes, benzol and alcoholic tars.

**Keywords:** Trice-oil emulsions; Asphaltenes ; Haydite; Alcoholic tars; Raw meal.

### 1. Introduction

Qualification refinement of trice oil emulsions and oil-slime is one of the most important ecological problems in oil processing industry <sup>[1]</sup>. Contemporary techniques for oil emulsions purification from water and mechanical impurities are not always efficient, what makes it difficult to reprocess them on distillation columns. Supply of the distillation columns with raw material with high content of water leads to an unstable operating mode of the column, decrease in production quality, superfluous expenses for water refinement, and corrosion of the equipment. Additional problem are caused by the impossibility of long-time storage of oil-removing products because of the processes induced by emulsions' "aging", i.e. reactions of hydrocarbon condensation in presence of atmospheric oxygen, the light from inorganic impurities. The most resistant oil-removing emulsions exist in unbroken condition, have been circulating in the system of oil-removing products preparing for years, and constantly increasing their volume. Huge amounts of oil-slimes have been accumulated at some factories of the branch for their long-term operating period; part of these has been buried, what causes disastrous damage to the ecology.

The water at Krasnodar oil-reprocessing plant, after sewage purification from oil products and mechanical impurities, is used for the makeup of the recycling water supply system of the plant. Oil-slime is being accumulated in sedimentation drainage and consists mainly of resistant oil emulsions. The composition of oil-removing emulsions is described in table 1.

Table 1. Qualities of oil-slimes at Krasnodar oil-reprocessing plant.

№	Sampling point	Water, %	Mechanical impurities, %	Oil product, %
1	Upper layer	0,03	0,068	100
2	Drain pipe	54	10	36
3	Bottom layer	40	8	52

According to the table 1, trice oil emulsions are concentrated in the middle and bottom layers of the drainage, and for their complete separation a great deal of time and resources are required. Analysis of the existing trends in utilization methods <sup>[2-6]</sup> allowed prove, that the simplest and the most economically efficient method is the direct usage of oil-slimes without

phase separation with intensification of useful properties by means of different additives. One of the vastest application fields for trice oil emulsions is their usage as a raw material for the production of building materials.

## 2. Experimental section

According to the results of the research there have been set forward some technological solutions for the raw meal preparation for the production of bricks and haydite.

For the production of bricks and hydite we have used oil-slime, collected during the treatment of sewage and process waste water, which is a trick liquid of density 0.86 – 0.97 g/cm<sup>3</sup>(№ 2 and 3 in table 1), containing water, mechanical impurities and combustible fractions. Combustible fractions mainly consist of asphaltenes, benzol and alcoholic tars.

Thanks to the combustibles and mechanical impurities, which are contained in oil-slimes, they are combustible and thinning additives at the same time; moreover, water contained in oil-slime provides formation of extra porosity.

The proposed raw meal for bricks production contains the mixture of saw dust and oil-slime as combustible and thinning additives in mass ratio 1,0–3,5 with water content in oil-slime 50–60 %wt. and the following blending ratio, %wt.: Mixture of saw dust and oil-slime 13–15; clay–100.

Bricks from the proposed raw meal were produced as follows: oil-slime and saw dust were blended, mixed with dry ground clay and blended again till homogeneity; bricks were formed from the derived mixture by pressing, then dried at 100–150°C during 1–2 hours and baked at 1000°C during 1 hour; produced bricks were then cooled, tested for mechanical compressive strength according to GOST ГOCT 4734–81, cold resisting property according to GOST 7025–78; heat conduction coefficient was rated at ITEM–1M device according to TY standard 25–1175.127–85 [6].

There has been studied the quantity of additives, decrease and increase of mass ratio between saw dust and oil-slime, the amount of water contained in oil-slime, influence the quality. The results are provided in table 2.

Table 2. Quality of the produced bricks

Example №	Raw meal content, %wt.				Mechanical compressive strength, mPa	Cold resisting property, cycles	Apparent porosity, %	Heat conduction coefficient
	Clay	Blend of additives	Mass ratio saw dust/oil-slime	Water amount in oil-slime				
1	86	14	2.5	54	38.0	88	35	0.39
2	87	13	2.5	54	38.2	86	36	0.38
3	85	15	2.5	54	38.3	02	35.8	0.39
4	86	14	3.5	54	39.1	91	34.6	0.38
5	86	14	1.0	54	38.4	91	35.7	0.36
6	86	14	2.5	50	39.3	91	35	0.37
7	86	14	2.5	60	38.3	91	35.5	0.38
8	89	11	2.5		15.0	27	19.5	0.81
9	84	16	2.5	54	12.0	25	40	0.40
10	86	14	0.8	54	9.0	14	18	0.88
11	86	14	3.8	54	17.0	26	37	0.70
12	86	14	2.5	49	15.0	30	17	0.80
13	86	14	2.5	61	11.0	13	42	0.41
14	-	-	-	-	17.0	25	23	0.71

Produced items correspond to the requirements of the highest brick mark according to GOST 530-95 (ex. 1-7) and possess the highest rates on mechanical strength, cold resisting property and apparent porosity. Though, these rates drastically decrease in case of reduction of additives amount, as well as fall and raise of mass ratio between saw dust and oil-slime, and drop of water content in oil-slime. In case of increase of additives amount over the declared one and in case of big water quantity in oil-slime, through cracks (40-60 mm,

4-8 per brick) can be seen on stretching faces of bricks for their full thickness, what causes considerable decrease in mechanical strength.

The proposed method of haydite production includes clay rock grinding, addition of 10-15% wt. of oil-slime, heated to 80-90°C and containing 30-60 % wt. of water [7] for elastic, good stirred clayey mass and addition of water, which quantity is calculated according to the formula:

$$A = x - (y + 0.01 \cdot c \cdot g), \text{ where}$$

x – optimal water amount, contained in clayey batch: 16 – 20 %wt.,

y – quantity of water in clayey material, %wt.,

c – quantity of added oil-slime, %wt.,

g – water amount in oil-slime, %wt.

This method allows produce haydite with low apparent density and high strength. Oil-slime is used as bloater. Being heated, oil-slime foams immensely, what extends its surface and allows spread over the clay surface as a thin film and penetrate into its pores.

At grains' baking clay expands at the expense of burning-out of organic components of oil-slime, as well as water vapors, which are either pore-forming material or catalyst of the processes, occurring during expansion of adobe grains.

In case of quick baking, complete burning-out of carbon with escape of gaseous oxidation products, such as carbonic oxide and dioxide (vaporescents) may be achieved only after completion of dehydration process and availability of free access of oxygen to the particles of the material.

In order to provide favorable deoxidizing atmosphere inside particles of the material, the baking curve should be set appropriately to shift the final oxidation (burning-out) of carbon residue of organic substances to the temperature zone at the beginning of expansion, what can be achieved by means of supply of adobe grains to the kiln with quite a definite humidity. The most optimal humidity is water content in clayey batch 16 – 20% wt.

### 3. Results and discussion

Tests were carried out in the following way: clayey material was delivered to loosening, then oil-slime, heated to 80 – 90°C, was added to it, containing 30 – 60 %wt. of water, and design water amount, mixing and forming of adobe grains, which were dried at 200°C, baked and cooled.

Definition of apparent density was made, as well as pressing strength in cylinder and visual parameters according to GOST 9758 – 86 and 9750 – 83.

It is well know, that temperature and water amount influence the apparent density and strength of haydite. On the basis of this oil-slime was heated to 75, 80, 90, 95, and 100°C. Water amount was 28, 30, 45, 60, 62 %wt. The results achieved are listed in table 3.

According to the data provided, the proposed method allows produce haydite with low apparent density of 330 – 345 kg/m<sup>3</sup> and high strength of 1, 49 – 1, 52 mPa (example № 1 - 5).

At oil-slime heating below the declared temperature the apparent density of haydite increases, and pores at fracture are only of small and medium size. At the increase of oil-slime heating over 95°C the quality of haydite gets better, and excessive pressure arises in camera for oil-slime heating (0,1 atm), what requires extra equipment for the camera according to safety specifications.

When water content in oil-slime is below 30 % wt., low airing of oil-slime is observed, its adhesion to the clay falls and the quality of the produced haydite declines, and in case of water growth in oil-slime above the declared level, at baking a powerful outcome of water vapors out of grain center is observed, and air void appears inside the grain. At haydite production the optimal water amount in the batch is of great importance. Humidity excess in adobe grains decreases the effect of pores formation, leads to cracks on the surface, impairs the structure of haydite, and enhances the apparent density.

Lack of humidity causes distress of grains in the process of baking, premature burning-out of organic substances, as a result of what high output of small, badly expanded haydite fractions occurs.

Table 3. Quality of produced haydite

Example №	Properties of oil-slime		Optimal water amount, % wt.	Properties of haydite		
	Heating temperature, °C	Water amount, % wt.		Apparent density, kg/m <sup>3</sup>	Strength, mPa	Visual parameters
1	90	45	18	340	1.52	Well expanded, has many medium and large pores. Grains were not cohered.
2	80	45	16	335	1.51	The same
3	95	45	20	345	1.50	«-»
4	90	30	18	330	1.49	«-»
5	90	60	18	335	1.49	«-»
6	100	45	18	340	1.51	As in Example № 1
7	75	45	18	360	1.45	Well expanded, surface is rough, pores are small and medium
8	90	28	18	275	1.49	Badly expanded, surface are covered with deep cracks, pores are small.
9	90	62	18	440	1.50	Mean expanded, pores are small and medium, grains are hollow, surface is cracky.
10	90	45	15	620	620	Distress of grains, many small badly expanded fractions (approximately 30 % mas.)
11	90	45	21	570	570	Cracks on the surface, pores are small in incipience.
12	-	30	-	365	365	Well expanded, many medium and small pores, cracks on the surface.

#### 4. Conclusion

According to the experiments carried out, the technology of oil-removing product use for bricks and haydite production allows:

- efficient use of oil-removing emulsion,
- production of bricks corresponding to the requirements of highest brick mark according to GOST 530-95, possessing high rates of mechanical strength, cold resisting property and apparent porosity,
- production of haydite with low apparent density 330 – 345 kg/m<sup>3</sup> and high strength 1, 49 – 1, 52 mPa,
- wasteless technology of oil-removing products reprocessing,
- diminish greatly detrimental effect of oil refinery on the environment.

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