

## ON THE PROCESS OF PHOSPHATE IONS REMOVAL FROM COTTREL MILK

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### ABSTRACT

*The investigation reported is focused on the processes of phosphate ions removal from cottrel milk by surface-active substances. It is found that oxyethylidenediphosphonic acid is very efficient as its application decreases phosphate ions content but increases that of cyanide anions.*

*It is shown that phosphanol and oxyethylidenediphosphonic acid show a selective complexing ability in respect to phosphate but not to cyanide containing compounds. Phosphanol requires less time for complex compounds formation than oxyethylidenediphosphonic acid, but they are less stable. Oxyethylidenediphosphonic acid forms complex compounds with cyanides within a prolonged contact with the cottrel milk liquid phase containing phosphate.*

*Diatomaceous earth is less effective in the purification of the milk liquid phase because of its high sorptive capacity for phosphate and cyanides. The advantages of phosphanol and oxyethylidenediphosphonic acid are verified.*

*Keywords: phosphoric production wastes, cottrel milk, cyanides, phosphates, surfactants, kieselguhr, phosphanol.*

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### INTRODUCTION

Nowadays several million tons of wastes are collected in dumps and storages of the phosphoric enterprises producing yellow phosphorus in the Republic of Kazakhstan. The phosphoric enterprises turn to be incompatible with the environment and are sources of significant amounts of toxic emissions, harmful solid and fluid wastes.

The main waste products of the phosphorus production refer to phosphoric slimes, cottrel dust, cottrel milk, ferrophosphorus, sewage and gas emissions of phosphoric furnaces. They contribute to about 10 % - 20 % of the feed stock losses.

The trapped cottrel dust has a chemical composition which depends on the feed stock structure and the technology applied. It contains not only polyphosphates [1, 2] but also toxic substances as cyanides, fluorides, etc.

The cottrel dust of the electric filters is removed in the form of a water suspension – cottrel milk (CM) with a density of 1,2 g/cm<sup>3</sup>. CM density depends on the mineral constituents of its solid phase. The chemical

composition of CM samples (in terms of solid residue) refers predominately to (mass %): 38 - 42 P<sub>2</sub>O<sub>5</sub>; 9,5 - 10,7 CaO; 7,2 - 9,8 K<sub>2</sub>O; 2,5 - 3,0 MgO; 1,9 - 3,9 Na<sub>2</sub>O; 3,5 - 4,1 R<sub>2</sub>O<sub>3</sub>; 2,1 - 2,5 F; 1,1 - 1,5 H<sub>2</sub>O.

The structure and properties of CM depend not only on the quality of the phosphatic raw materials, the conditions of their pretreatment, the mode of the oven unit, but also to a significant extent on the formed suspensions pH. Thus CM obtained on the ground of lumpy raw materials, with suspensions pH of 7 contains from 12,6 mg/l to 218 mg/l of cyanides. CM formed in the course of pellets processing is in the form of a suspension whose pH varies between 7 and 12, while the cyanides content is in the range of 110,3 mg/l - 9450 mg/l. The highest content of cyanides of 9000 mg/l is observed at pH value of 12. Thus pH increase is an especially important factor determining production of CM rich in cyanides.

Methods of ferrocyanides production on the ground of CM are described in a number of previous papers. However, the high content of phosphate ions in CM exerts a negative impact on the process of pigments synthesis. That is why the phosphate ions removal from CM is a problem

of primary importance aiming an increase of the yield and the quality of the ferrocyanide pigments produced. The present communication is focused on its solution.

## EXPERIMENTAL

### Materials

The following materials were used: phosphanol (boiling point 48°C/mm – 49°C/mm, melting point 12°C,  $n_{D,20}^{20}$ ,  $d_{4,20}^{20}$ ); oxyethylidenediphosphonic (OEDP) acid (boiling point 198°C-200°C,  $\Delta H_{\text{evaporation}}^0$  of 350 kJ/kg,  $\Delta H_{\text{combustion}}^0$  of - 1214 kJ/mol,  $\Delta H_{\text{formation}}^0$  of - 2177 kJ/mol, water solubility - 2300 g/l); kieselguhr of 0,01 mm - 0,02 mm size,  $\rho$  of 2000 - 3000 kg/m<sup>3</sup>, porosity of 60,2 % - 64 %, hardness 1-3; H<sub>2</sub>SO<sub>4</sub> (pure, GOST 4204-77); KOH (pure, GOST 4328-77); distilled water (GOST 6709-72); CM liquid phase of pH 14, density of 1,2 g/cm<sup>3</sup> and a chemical composition (mass %) of : 0,73 - 14,5 P<sub>2</sub>O<sub>5</sub>; 0,05 - 0,35 CaO; 14,17 - 15,53 K<sub>2</sub>O; 1,91 - 2,72 Na<sub>2</sub>O; 0,01 - 0,02 MgO; 4,62 - 5,05 SO<sub>4</sub><sup>2-</sup>; 1,52 - 2,60 Fe; 960 mg/l - 3942 mg/l CN<sup>-</sup>).

### Methods

The ferrocyanides determination was carried out by titration using a zinc sulfate solution in presence of diphenylamine and potassium ferrocyanide.

The cyanides content was determined by titration with nickelous nitrate solution in a weak ammonia medium using dimethylglyoxime [2] as an indicator.

The presence of iron ions was determined by a photocolometric method in correspondence with GOST 10678-76.

The phosphorus content was identified by a colorimetric method on the ground of yellow phosphovanadic complex absorption, while that of P<sub>2</sub>O<sub>5</sub> - by the weight citrate method of Bekterov-Wagner.

The pH values were measured on a brand pH-meter 410.

The following physical methods were applied:

X-ray diffraction method. A diffractometer “DRON-3” was used. The identification of the crystalline products was carried out through a comparison with literature data.

IR analysis. An infrared spectrophotometer Nikolet 5700 was used. The range studied referred to that from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The identification of the samples was carried out on the ground of juxtaposition with IR spectra

of the individual compounds and literature data [6 - 14].

The CM filtrate contained up to 14,5 % of P<sub>2</sub>O<sub>5</sub>. As its impact on iron ferrocyanide synthesis process was negative a pre-refining was carried out. 10 % solutions of diatomaceous earth, phosphanol and OEDP acid were used to precipitate the phosphate ions present [3]. The choice of precipitants was determined by their indifference to cyanides, which in turn provided concentration of the cyanide containing components in CM filtrate.

CM purification from phosphates using the precipitants pointed above was carried out under stirring at an ambient temperature. The precipitant effectiveness was determined on the ground of the residual content of phosphates and CN-ions in the filtrate taking into consideration the contact time as well.

The spectrophotometric method was applied to study the process of a complexation of potassium ferrocyanides with the surface-active substances present in the aqueous medium.

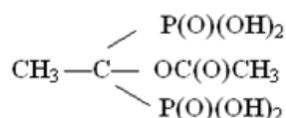
The structure of the absorbing particles was determined with the application of the method of isomolar series and molar ratios [4, 5]. The latter referred to the introduction of different quantities of a given component to a constant amount of a selected component of the system aiming to reach the chosen ratio between them. The total volume was adjusted to 100 mL by adding water. The systems prepared were studied in a wide range of pH values (1 - 10) achieved through introduction of a sulfuric acid solution.

The equilibrium state of the systems studied was attained as follows. The solutions of the initial components taken in the ratios envisaged were stirred within an hour in a thermostat at a temperature of 25°C. Then they were left undisturbed at the same temperature to provide the sedimentation expected. An aliquot part of the transparent solution obtained was taken for an analysis.

## RESULTS AND DISCUSSION

The important property of the surface-active substances (SAS) from the practical point of view is that the adsorbing molecules (ions) of the surfactant have a specific structure [4] - they contain a polar group and a non-polar hydrocarbon radical. The latter has a surface activity in respect to the non-polar phase. It is known that even in a case of an insignificant content of SAS in an aqueous salt solution (0,01 mass % - 0,1 mass %)

the interfacial tension decreases providing emulsion formation. The application of SAS is determined by their surface activity, their adsorption layers structure and bulk solutions properties. SAS find a wide application in regulating the structurization and stability of the disperse systems with a fluid dispersion medium (an aqueous and organic one). The phospho-organic compounds and especially the derivatives of phosphoric and oxyphosphoric acids used as extracting agents and surfactants attract a specific attention [4]. OEDP acid and phosphanol which refer to the chelate forming compounds present the highest interest. They are rather stable. For example, OEDP acid decays at 250°C, while in an aqueous solutions – at 140°C. It refers to the strong acid



in whose molecule phosphorus is directly bonded to carbon. OEDP acid and phosphanol are characterized by a complexing activity. Thus OEDP acid forms steady complexes with cations of alkali-earth metals. Furthermore, OEDP acid and phosphanol show a cationic and an anionic activity [5] in solutions.

According to CM chemical analysis  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  as well as  $\text{PO}_4^{3-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$  are found in its liquid phase. Purification of such multicomponent system can efficiently proceed in presence of SAS described above.

Kieselguhr (diatomaceous earth) attracts attention in case of phosphates precipitation. It is a fine-pored material consisting mainly of silicon dioxide. Based on its adsorptive properties it is used in filtering and as a catalyst carrier. A colloidal solution is formed in the course of its dissolution in water which in fact provides its treating as a colloid surfactant.

This section reports the experimental results obtained in phosphates elimination from CM liquid phase by using phosphanol, OEDP acid and kieselguhr. The liquid phase containing 0,73 % of  $\text{P}_2\text{O}_5$  and 960 mg/l of  $\text{CN}^-$  ions has pH of 12 and a density of 1,03 g/cm<sup>3</sup>.

The process of purification is carried out at ambient temperature (25°C). The procedure used is as follows. 10 % surfactant solution is added to CM filtrate in CM:SAS ratio of 100 mass parts : 2,5 mass parts. The mixture formed is stirred and filtered. The phosphate ions content in the form of  $\text{P}_2\text{O}_5$  is determined in the filtrate. The content of  $\text{CN}^-$  ions is also followed as the surfactants chosen are applied for the first time to CM cleaning, and besides its purified liquid phase is further used for iron ferrocyanide production. Furthermore, it is found that the duration of the purification process has a significant effect not only on phosphates residual content, but also on cyanide ions presence.

Table 1 and Fig. 1 illustrate the results referring to the content of residual  $\text{P}_2\text{O}_5$  and  $\text{CN}^-$  in the filtrate obtained in case of CM treatment with phosphanol. The effect of the contact time varying from 15 min to 60 min is outlined.

It is seen that  $\text{P}_2\text{O}_5$  presence in the filtrate depends directly on the contact time. The latter increase brings about an increase of  $\text{P}_2\text{O}_5$  removal. The best results in this respect are obtained in case of 15 min treatment as  $\text{P}_2\text{O}_5$  content in the filtrate decreases 9,1 times when compared to the initial one. Only 1,26 times decrease is observed within 60 min contact time. It is worth adding that cyanide anions content increases in presence of phosphanol - 1,04 times after 20 min contact and 1,37 times in case of 60 min treatment of CM. This can be most probably attributed to the sedimentation of phosphates and other impurities which in turn results in cyanide ions concentration increase in the filtrate.

Table 1. Content of  $\text{P}_2\text{O}_5$  and cyanide anions in the liquid phase of CM treated with phosphanol (the initial concentrations of  $\text{P}_2\text{O}_5$  and cyanide anions refer to 0.73 % and 960 mg/L, correspondingly).

Time, min	$\text{P}_2\text{O}_5$ , %	$\text{CN}^-$ , mg/l
15	0,08	962
20	0,11	998
30	0,20	1090
40	0,34	1170
50	0,42	1248
60	0,58	1315

Another series of experiments is carried out under identical conditions but with the participation of OEDP acid. The data obtained is presented in Table 2 and Fig. 2.

In this case the contact time increase leads to

decrease of the content of  $P_2O_5$  and  $CN^-$  but the latter presence is higher than that of the initial liquid phase of CM. For example, the amount of  $P_2O_5$  obtained within 20 min of contact decreases by 0,12 %. The values re-

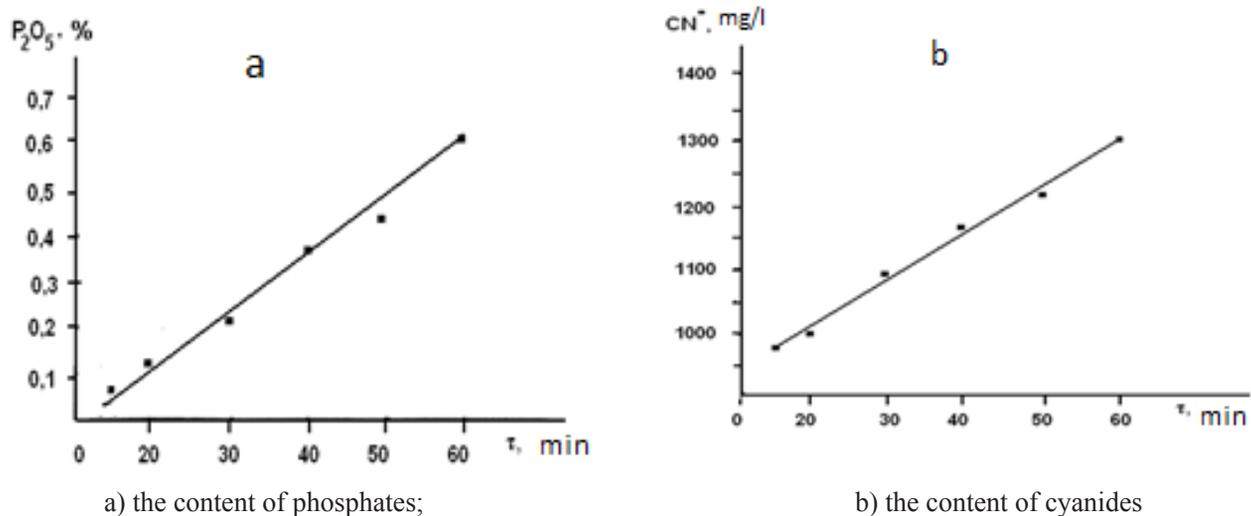


Fig. 1. Effect of the contact time on the content of  $P_2O_5$  (a) and cyanide anions (b) in case of CM treatment with phosphanol.

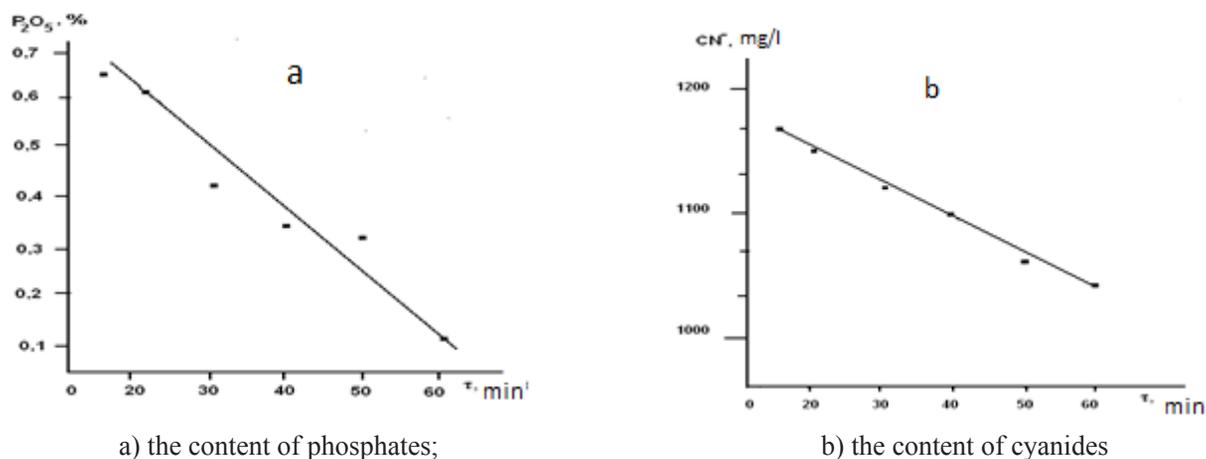


Fig. 2. Effect of the contact time on the content of  $P_2O_5$  (a) and cyanide anions (b) in case of CM treatment with OEDP acid.

Table 2. Content of  $P_2O_5$  and cyanide anions in the liquid phase of CM treated with OEDP acid (the initial concentrations of  $P_2O_5$  and cyanide anions refer to 0.73 % and 960 mg/L, correspondingly).

Time, min	$P_2O_5$ , %	$CN^-$ , mg/l
15	0,65	1165
20	0,61	1155
30	0,43	1122
40	0,34	1100
50	0,31	1064
60	0,12	1048

ferring to the experiments with 30 min and 50 min of contact time are 0,30 % and 0,42 %, correspondingly. The respective cyanide anions concentrations refer to 195 mg/l, 162 mg/l, 104 mg/l. The increase observed is most probably connected with the coprecipitation of the phosphates and the impurities present in CM. However, it is evident that the contact time increase starts to result in  $\text{CN}^-$  concentration decrease. Thus, the value reached within 15 min of treatment is 205 mg/l, while that found after 60 min of contact time is only 88 mg/l. This concentration decrease could be explained with the increased cyanide anions complexation in presence of OEDP. That is, the latter participation is rather efficient in respect to the phosphates. Besides, no decrease of cyanide anions content is observed.

The corresponding experimental results obtained in presence of kieselguhr are presented in Table 3 and Fig. 3.

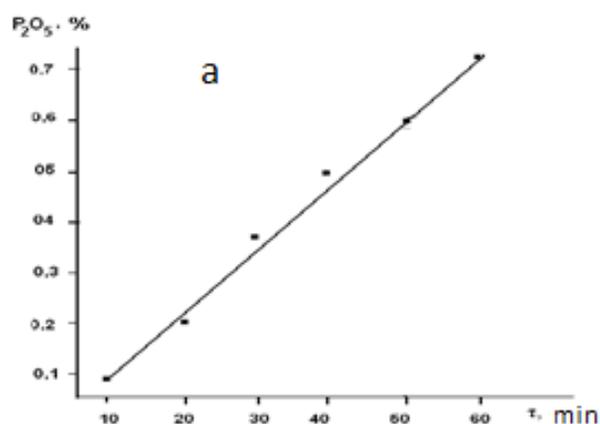
The dependences observed are identical in respect to  $\text{P}_2\text{O}_5$  and cyanide anions – the concentration of both products increase with the contact time increase. Ac-

cording to the results obtained in case of a short treatment time (less than 10 min) the adsorbent is effective in respect to the phosphate and the cyanide anions, which in fact bond to its surface as a result of physical adsorption. The increase of the contact time brings about desorption, i.e. a transfer of the adsorbates back to the solution starts to take place. This leads to the simultaneous increase of the concentration of  $\text{P}_2\text{O}_5$  and  $\text{CN}^-$  ions in the filtrate. Thus the  $\text{CN}^-$  ions content of the filtrates obtained in case of a contact time of 20 min and 60 min amounts to 42 mg/l and 162 mg/l, correspondingly, when compared to that found after 10 min treatment. But their concentration obtained in case of 60 min treatment does not exceed the initial one in crude CM. That is, kieselguhr shows good adsorptive properties both in respect to phosphates and to cyanide anions within the first 15 min of the process.

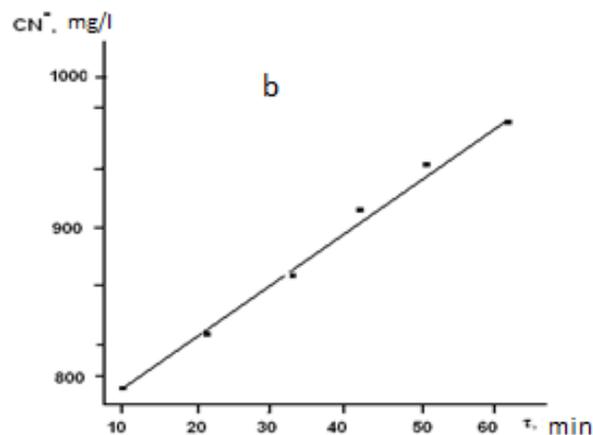
The comparative analysis of the sorbents effectiveness presented in Table 4 shows that phosphanol and kieselguhr provide 89 % phosphate content decrease

Table 3. Content of  $\text{P}_2\text{O}_5$  and cyanide anions in the liquid phase of CM treated with kieselguhr (the initial concentrations of  $\text{P}_2\text{O}_5$  and cyanide anions refer to 0.73 % and 960 mg/L, correspondingly).

Time, min	$\text{P}_2\text{O}_5$ , %	$\text{CN}^-$ , mg/l
15	0,08	788
20	0,20	830
30	0,37	870
40	0,50	919
50	0,61	945
60	0,72	950



a) the content of phosphates



b) the maintenance of Cyanidums

Fig. 3. Effect of the contact time on the content of  $\text{P}_2\text{O}_5$  (a) and cyanide anions (b) in case of CM treatment with kieselguhr.

within the first 10 min of the contact with CM. At the same time kieselguhr shows an extent of cyanide anions sorption amounting to 17,92 %, while phosphanol concentrates cyanide anions containing components. The extent of CN<sup>-</sup> ions concentration increase reaches a value of 0,21 % in respect to the initial one within 15 min of treatment.

It is worth noting that the addition of phosphanol to CM liquid phase results in phosphate removal but the effect decreases with increase of the contact time. These changes take place simultaneously with the decrease of cyanide anions concentration. The use of kieselguhr results in decrease of cyanide anions losses, but does not provide a high extent of P<sub>2</sub>O<sub>5</sub> elimination. For example, the extent of P<sub>2</sub>O<sub>5</sub> removal in presence of phosphanol is

equal to 42,47 %, while the extent of cyanide anions concentration amounts to 30 % in case of 50 min contact time of the filtrate with phosphanol. The corresponding values obtained in presence of kieselguhr refer to 16,44 % and 1,56 %, correspondingly.

OEDP acid is a rather efficient in phosphates precipitation and cyanide containing compounds concentration in case of a prolonged contact time. Thus the 10 min contact results in 11 % removal of P<sub>2</sub>O<sub>5</sub> and increase of CN<sup>-</sup> ions concentration to 21,4 %. The 60 min treatment brings about effects amounting to 83,56 % and 9,17 %, correspondingly. That is, OEDP acid provides a high (83,56 %) extent of P<sub>2</sub>O<sub>5</sub> removal together with increased cyanide anions concentration (to 9,2 %) only in case of a prolonged treatment.

Table 4. Effect of the sorbent nature and the contact time with CM liquid phase on the extent of phosphates removal and cyanide anions sorption.

Time, min	phosphanol		OEDP		kieselguhr	
	K <sub>pur</sub> P <sub>2</sub> O <sub>5</sub>	K <sub>s</sub> CN <sup>-</sup>	K <sub>pur</sub> P <sub>2</sub> O <sub>5</sub>	K <sub>s</sub> CN <sup>-</sup>	K <sub>pur</sub> P <sub>2</sub> O <sub>5</sub>	K <sub>s</sub> CN <sup>-</sup>
15	89,04	0,21	10,96	21,35	79,45	14,80
20	84,93	4,00	16,44	20,31	72,60	13,54
30	72,60	13,54	41,10	16,88	49,32	9,38
40	53,42	21,88	53,42	14,58	31,51	4,27
50	42,47	30,00	57,53	10,83	16,44	1,56
60	20,55	36,98	83,56	9,17	1,37	1,04

where:  $K_{pur} P_2O_5 - \text{Extent of } P_2O_5 \text{ removal} = \frac{P_2O_5_{pur CM}}{P_2O_5_{ex}} \cdot 100 \%$   $K_s CN^- - \text{Extent of } CN^- \text{ sorption} = \frac{CN^-_{pur CM}}{CN^-_{ex}} \cdot 100 \%$

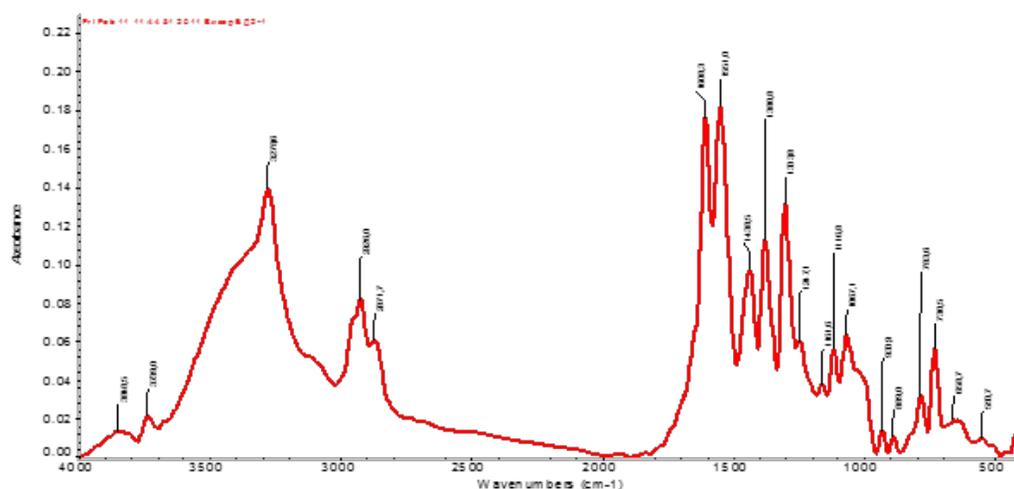


Fig. 4. IR spectroscopic analysis of the solid residue obtained after CM liquid phase purification carried out with OEDP acid.

The apparent distinctions in the properties of the surfactants studied are explained with their nature.

As kieselguhr is a natural silicate clay mineral it shows sorptive properties both in respect to cyanide anions and phosphate. Besides physical adsorption takes place. The increase of the contact time brings about phosphate and cyanide anions desorption.

The IR spectrum of the solid residue obtained after CM liquid phase purification carried out with kieselguhr shows frequencies ( $551\text{ cm}^{-1}$ ;  $597\text{ cm}^{-1}$ ;  $1016\text{ cm}^{-1}$ ;  $1063\text{ cm}^{-1}$ ;  $1166\text{ cm}^{-1}$ ) characteristic for  $\text{Ca}_3(\text{PO}_4)_2$  and bands of a weak intensity at  $1384\text{ cm}^{-1}$  and  $3391\text{ cm}^{-1}$  which refer to  $[\text{Fe}(\text{CN})_6]^{4-}$  vibrations. The IR spectra of the solid residue obtained after CM liquid phase treatment with phosphanol and OEDP acid (Fig.4) indicate the presence of  $\text{Ca}_3(\text{PO}_4)_2$  outlined by intensive bands recorded at  $1067\text{ cm}^{-1}$ ,  $1380\text{ cm}^{-1}$  and  $1551\text{ cm}^{-1}$  [6 - 14].

## CONCLUSIONS

Phosphanol and OEDP acid are derivatives of oxophosphonic acid. The comparison of their structure shows that they have identical alcoholic and similar acidic groups. That is why they have close physical and chemical properties. They are applied as extract agents and softeners. The phosphorus containing groups present in phosphanol and OEDP acid have a variable valency and which is why they can form complex compounds with phosphate- and the cyanide containing compounds in CM.

However phosphanol and OEDP acid show a selective complex compounds formation ability in relation to phosphate when compared to that in respect to cyanide containing compounds. Besides phosphanol apparently requires less time to form complexes, but they are less stable. OEDP acid forms complex compounds not only with the phosphates, but with the cyanide containing compounds as well in the course of a prolonged contact time. This leads to cyanides concentration decrease.

The investigation carried out shows that kieselguhr is less effective in the process of cottage cheese milk purification because of the high sorption ability shown both in respect to phosphate and cyanide anions. It follows that phosphanol and OEDP show better prospects. The contact time in presence of phosphanol should not exceed 10 min - 15 min, while that in presence of OEDP acid is expected to be at least 60 min.

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