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## EXPERIMENTAL ANALYSIS OF CHEMICAL DEMULSIFICATION OF CUTTING OIL

### Abstract

The wastewater produced by the metal industry is often present in the form of oil-in-water (O/W) or water-in-oil (W/O) emulsions. These fluids contain a certain amount of valuable oil that can be recovered in the recycling process. Therefore, the development of novel, efficient, and low cost processes for the treatment of metalworking fluid is necessary. Demulsification to separate oil/water mixtures is a very interesting option because it allows the recovery and reuse of the lubricant oil and effects in cleaner, easily treatable wastewater. Chemical destabilization is the most common way of demulsification of metalworking fluids. As an example, inorganic salts can be used as demulsifiers. In the presented work the efficiency of treatment of cutting emulsions with chemical demulsification with usage of aluminum sulfate (IV) is described. The emulsion was prepared with Emulgol-ES12 self-emulsifying oil delivered by Orlen S.A. In the research the feasibility of the demulsifier was checked. The novel in this paper is determination of the optimal dosage of emulsifier using the TurbiscanLab<sup>®</sup> apparatus. It is relatively quick and precise method that can be applied in the industry.

### Key words

demulsification, emulsion, TurbiscanLab, cutting oil

### Introduction

Emulsions of cutting fluids are metalworking fluids (MWFs) that are being used in metal-mechanical industries to aid cutting processes, to prevent corrosion, and to improve lubrication, cooling, surface cleaning, and tool life. When used in machining processes, these emulsions lose their properties and effectiveness due to thermal degradation and contamination[1]. The replacement of these fluids leads to the occurrence of stable waste emulsions that can be hazardous to the environment [2,3,4,5]. Cutting fluids are usually composed of mineral oil (40-80 wt.%), a surfactant, and additives. The additives are present in the mixture to meet the specifications for commercial concentrates, such as resistance to bacterial growth and low corrosion capacity. Additionally, some cutting fluids may contain water in their composition [2,5,6].

The lifecycle of cutting fluids in a machining facility involves four stages [7]:

- storage and handling
- mixing with water
- process using
- disposal

After the using stage, cutting oils, normally in the form of oil-in-water emulsion, will consist of different contaminants, such particles, heavy metals, and organic matters. These rejected oils are typically handled by two methods. The first one is recycling, during which contaminants are separated from the rejected oil, and then purified before returning to use in the manufacture process. Separation process can be operated by a variety of physical processes: separation by magnetic or centrifugal force, filtration or sedimentation. After this stage, the oils are purified to adjust their properties. As an example, oil can be heated to reduce viscosity. Sterilization is also significant process for protecting against infection to eliminate bacteria, which might be present in the oil. Another process used with rejected oil is disposal. This method is applied when oil recovery is not possible or difficult. This can happen when emulsion presents high water content or inadequate quality in the recovered oil. The disposal process is in two stages. First, the oil emulsions are destabilized into oil and water, normally by chemical processes. According to Rios et al. [5], inorganic salts can be employed as coagulants to demulsify the emulsion, leading to the coalescence of oil droplets. The separated oil is then used as an alternative fuel. However, biodegradation is another interesting alternative. Cheng et al. [3] reviewed that the biological degradation, both aerobic and anaerobic, and stated that it can effectively remove COD and

turbidity, which represent the amount of cutting oil in water. Electro-coagulation is another process that can be applied for treatment of metalworking fluid as well [8,9]. Methods of demulsification of oil in water emulsion are presented in Table 1.

Table 1. Demulsification methods of metalworking fluids

Demulsification method	Described by
1. With inorganic salts	Rios et al.(1998)
2. Biodegradation	Cheng et al.(2005)
3. Electrocoagulation	Bensadok et al.(2007)

Source: Author's

Residual cutting fluids have a high carcinogenic potential due to the presence of products derived from the degradation of additives, polycyclic aromatic hydrocarbon (PAH), nitrosamines, among others [10]. According to Soković and Mijanović [11], secondary substances that are formed using cutting fluids include reaction products, foreign bodies, and microorganisms. It is essential to treat the cutting fluid wastewaters before its disposal in the environment considering the risks and the presence of strict environmental regulations. For example, the directive 2000/76/EC of the European Union defines a limit on the amount of used metalworking fluids that can be disposed of by incineration. Therefore, the development of novel, efficient, and low cost processes for the treatment of metalworking fluid is necessary [3, 12,13,28].

As it was mentioned, there are many methods of utilization of used cutting fluids. In chemical methods, it is possible to use salts such as alum or ferric salts [5,14]. The advantages of this method are low investment costs and the possibility of a wide range of applications. The measurement necessary for demulsification consists of a tank filled with emulsion, a stir and a pump for demulsifier. Operation costs depends mainly on the price of demulsifiers. The disadvantage of this method is fact that it is difficult to adjust the type and amount of used demulsifier [15]. Therefore, in this article we also focused on the determination of the optimal dosage of the emulsion breaking agent.

Chemicals that are generally used to for destabilization of cutting oils emulsions are described below [16]:

- Monovalent electrolytes
- Bivalent electrolytes
- Multivalent electrolytes
- Surfactants with opposite charge

In experiments, the TurbiscanLab<sup>®</sup> was used. It is an optical measurement device that allows to monitor the emulsion behaviour in real time. The apparatus uses a multiple light scattering analysis technique [18,19,20]. TurbiscanLab<sup>®</sup> can be used to monitor the reversible degradation processes such as creaming and sedimentation and irreversible ones such as coalescence and aggregation. This apparatus can detect the changes in structure of fluid before they can be visible to human eye [20]. Analysis of transmittance signal and back scattering signal is recorded in time. This allows to monitor the real time stability of fluid. This device is used in the chemical industry [18] as well as in the pharmaceutical industry [20]. Up to now, not many articles present the analysis of demulsification with a TurbiscanLab<sup>®</sup> device. However, it is possible that this apparatus can be used to conduct a precise analysis of the emulsion degradation processes [21,23,26,27].

The aim of this work is to analyse the degradation mechanisms of 4% and 8% oil in water emulsion based on EMULGOL ES 12 oil delivered by Orlen S.A. This concentration has been chosen since they are most popular in industry. During the analysis, we used aluminium sulphate with a concentration of 8g/l to conduct demulsification. To analyse kinetics of phase separation the TurbiscanLab<sup>®</sup> apparatus was used. The method uses novel equipment to correctly determine the amount of necessary demulsifier for emulsion breakage. It is quick and simple method that can be broadly introduced in the industry. The conducted experiments are very important for metal-mechanical employees. As an example, presented research can be used as a short guide in demulsification of metalworking emulsions.

### Materials and methods

In a 250ml baker we prepared 100ml emulsion based on emulsifying oil EMULGOL ES-12 delivered by Orlen S.A, by mixing mentioned oil and water with a hand homogenizer for 120 seconds. In Table 2 we present the type of emulsion prepared, Table 3 shows the percentage composition of the emulsion system, and Table 4 represents the used demulsifier.

Tab.2. Specification of used emulsion

Emulsion type	Dispersed phase	Continuous phase
oil-in-water (O/W)	Emulsifying oil Emulgol ES-12	Tap water

Source: Author's

Tab.3. The concentration of used emulsion

Water amount	Oil amount	Concentration of emulsion
96ml	4ml	4%
92ml	8ml	8%

Source: Author's

Tab.4. Type and amount of used demulsifier

Demulsifier type	Demulsifier concentration	The amount of used demulsifier
aluminium sulfate $Al_2(SO_4)_3$	8g/l	4ml/10ml emulsion 4% 6ml/10ml emulsion 4% 6ml/10ml emulsion 8% 8ml/10ml emulsji 8% 10ml/10ml emulsji 8%

Source: Author's

In Fig. 1 we present the picture of Turbiscan Lab scanning device with measuring principle.

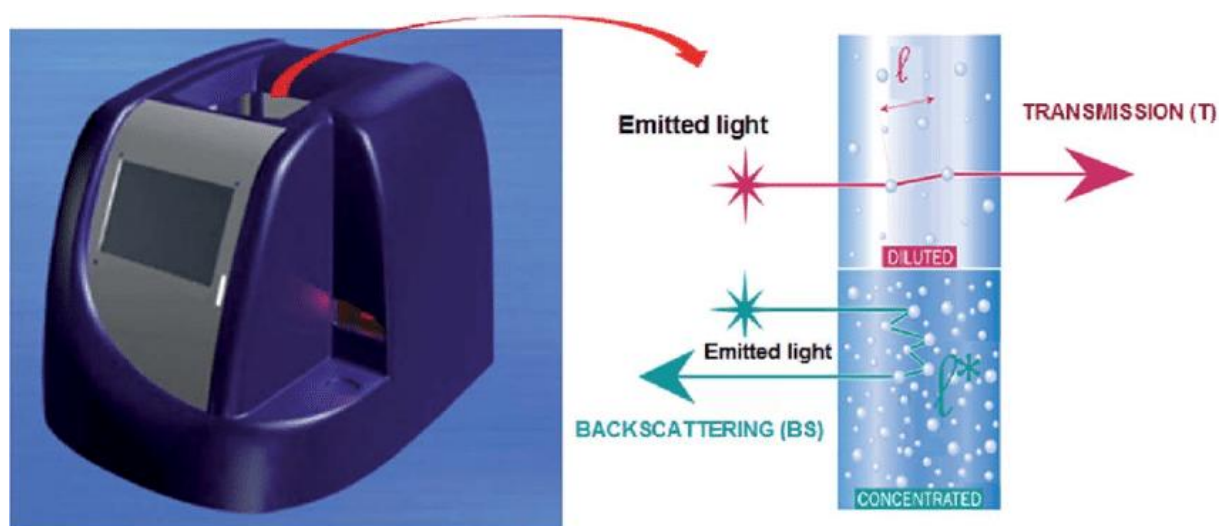


Fig. 1. Turbiscan Lab and its measuring method

Source: [17]

In order to separate phases in previously prepared systems, we placed 10ml of emulsion in a measuring cell of the TurbiscanLab® device. After this, we added to it certain amount of demulsifier-4ml, 6ml, or 8ml with a syringe and mixed the system with a magnetic stirrer for 20 seconds. Then we inserted the measuring cell in the TurbiscanLab® apparatus and started the measurement. We set the device to scan a measurement cell

every 1 minute for the first hour, then every 5 minutes for two hours, and then every hour. The total time of a single experiment was 24 hours. To better understand the results of the experiment we also made visual observations of the samples.

### Results and discussion

In Fig.2 we presented the results of demulsification of 4% emulsion based on emulsifying oil Emulgol ES-12 after addition of 4ml of aluminum sulfate with concentration of 8g/l for 10ml of emulsion. In the picture, transmittance and back-scattering signal is presented. The time of measurement was 24 hours. It can be observed that the fastest changes are present in first three hours of the process. The lowering of the back scattering signal at that time means that coalescence occurred. It can also be noted that close to the bottom of the measurement cell the water layer is present just after a couple minutes. Therefore, the measurements need to be conducted just after the addition of demulsifier. It can be also noted that after 24 hours the demulsification process was not finished- the transmittance at cell height 20mm-28mm was still very little.

Our demulsification results are in common with the observations of Rios et al. [5], however we monitored emulsion for a longer period of time. Another deviation is that instead of nefelometric measuring device, we used more advanced turbidimetric technique. Our method is also more simple than electrocoagulation used by Bensadok et al. [2] and Kobya et al. [25]. Compared to work of Cheng et al. [3], who studied biological degradation, our approach eliminate significant difficulties in operating bioreactors, such as maintenance of the stability of the microbial communities present in activated sludge plants. Demirbas and Kobya [28] investigated processes of metalworking fluid wastewater chemical coagulation and electrocoagulation, however they focused mainly on operation costs. They also used emulsion based on Castrol oil, while we are using the one based on Emulgol, which is more popular in Europe.

In Fig. 3 we present the visual observations of the demulsification process. On the left side, we present the sample after ten minutes of demulsifier addition, and on the right side we show the same sample after 180 minutes of process. It can be observed that the clarity of the sample increased and at the top the oil layer is present. However, the visual analysis does not allow one to follow the mechanism of demulsification. Therefore, we state that turbidimetric analysis is more precise than visual observation and it allows to us to better understand the nature of demulsification.

In Fig. 4 we presented the results for the same emulsion as in Fig. 2, but in this case we added 6ml of aluminum sulfate for 10 ml of emulsion. As it can be observed, the transmittance signal increment is bigger than in Fig. 1. Also, the final signal is higher, which means that the separation process finished and oil is fully separated from water. During analysis of the back-scattering signal it is possible to observe the separation of the oil phase at the top of the sample, which results in a decrease of signal at this height.

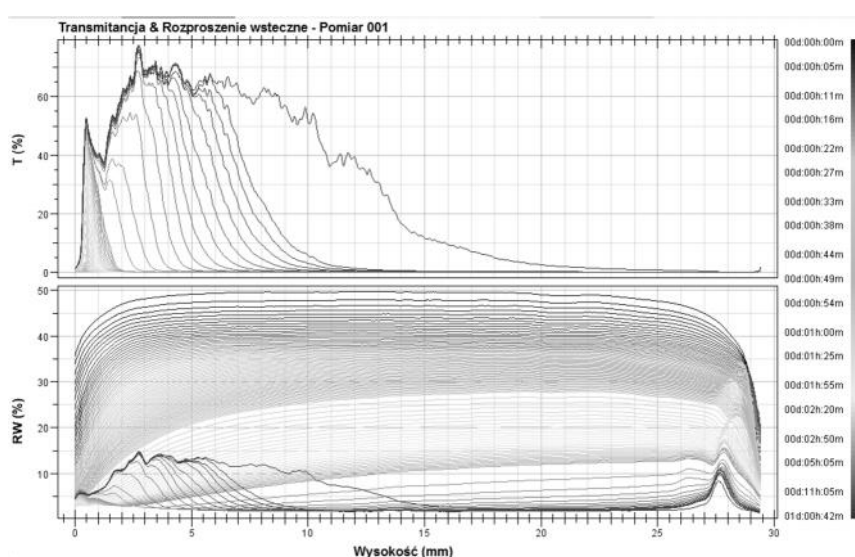


Fig. 2. Transmittance and back-scattering signal change in time versus height of the sample for 4ml of demulsifier addition for 10ml of 4% emulsion

Source: Author's



Fig. 3. On left- sample after 10 minutes of demulsifier addition. On right- sample after 180 minutes of demulsifier addition.

Source: Author's

Full separation of phases in the case of Fig. 2 was observed after 72 hours of demulsifier addition. In the case of Fig. 3, it took 24 hours to separate the water from the oil, which means that by that time all oil droplets moved to the top of measurement cell.

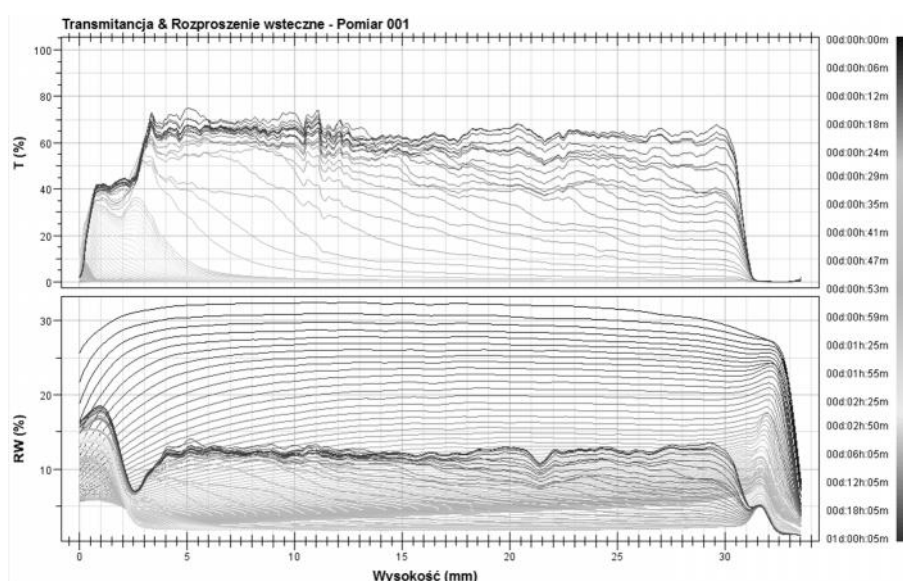


Fig. 4. Transmittance and back-scattering signal change in time versus height of the sample for 6ml addition of demulsifier for 10ml of 4% emulsion

Source: Author's

In Fig. 5 we presented the increment of transmittance in time for addition of 4ml and 6ml of aluminum sulfate for 10ml of 4% emulsion at 25mm height of measuring cell. As can be seen, the increase is gradual for the addition of 6ml. The sample reaches 70% of transmittance after 24 hours, which means that there is no oil left in water phase.

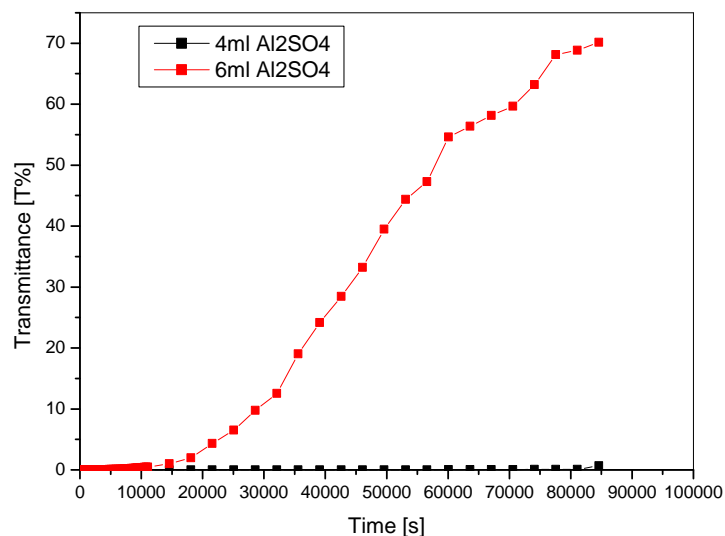


Fig. 5. Increment of transmittance for 4ml and 6ml addition of demulsifier for 10ml of 4% oil-in-water emulsion  
Source: Author's

In Fig. 6 we presented the change of the back-scattering signal over time for 6ml demulsifier addition for 10ml of emulsion with 4% oil concentration. It was read for 25mm height. As can be seen, the signal decreased and then increased. During first two hours, the signal value lowers, which is related to the coalescence of droplets. Then phases separate, and only tiny oil droplets are left in water phase. After three hours of process the signal increased again, which can be explained with Mie theory, according to which the increment of this signal is present when the oil droplets are very small- in case of TurbiscanLab® below 0,6 $\mu$ m [24].

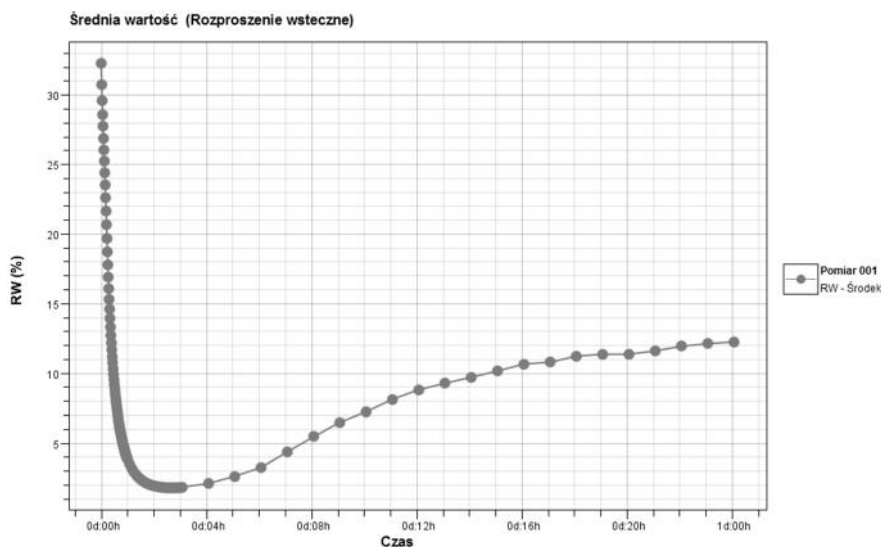


Fig. 6. Change of back-scattering signal at the middle of sample for 24 hours of process for 6ml demulsifier addition for 10ml of 4% emulsion  
Source: Author's

In Fig. 7 we presented results for analysis of separation of emulsion with 8% concentration, reading two times higher than before. For this experiment, we added 10ml of sample 6ml of aluminum sulfate with 8g/l concentration. As can be seen, the increment in transmittance is observed only at the bottom of the sample. It means that 24 hours was not enough time for the complete separation for this amount of demulsifier addition.

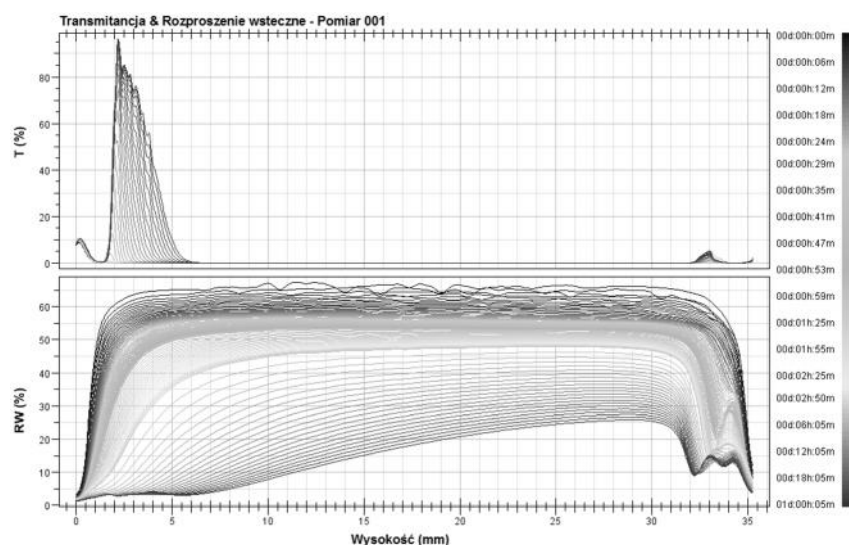


Fig. 7. Transmittance and back-scattering signal change in time versus height of the sample for 6ml addition of demulsifier for 10ml of 8% emulsion  
Source: Author's

In Fig. 8 we presented the transmittance and the back-scattering signal change for 8% emulsion overtime after the addition of 8ml demulsifier for 10ml of emulsion. From transmittance, it can be observed that the water phase was bigger than in the case of Fig. 7. However, the small value of this signal at a height of 25mm to 33mm suggests that the process did not complete in 24 hours. Probably a few more hours would be needed to finish the phase separation.

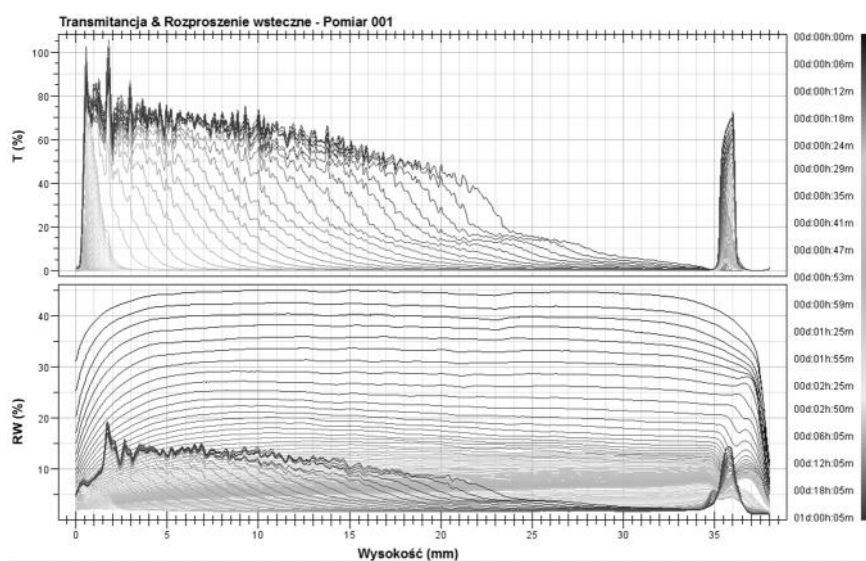


Fig. 8. Transmittance and back-scattering signal change in time versus height of the sample for 8ml addition of demulsifier for 10ml of 8% emulsion  
Source: Author's

In Fig. 9 we presented the transmittance and the back-scattering signal change for 8% emulsion overtime after the addition of 10ml demulsifier for 10ml of emulsion. In this case, the transmittance signal was smaller than after 8ml the addition of demulsifier. It means that the time needed for demulsification will be longer than for 8ml of additional emulsion breaker. Therefore, we state that 8ml addition of aluminum sulfate with 8g/l concentration is the optimal dosage for break 8% oil-in-water emulsion based on Emulgol ES-12.

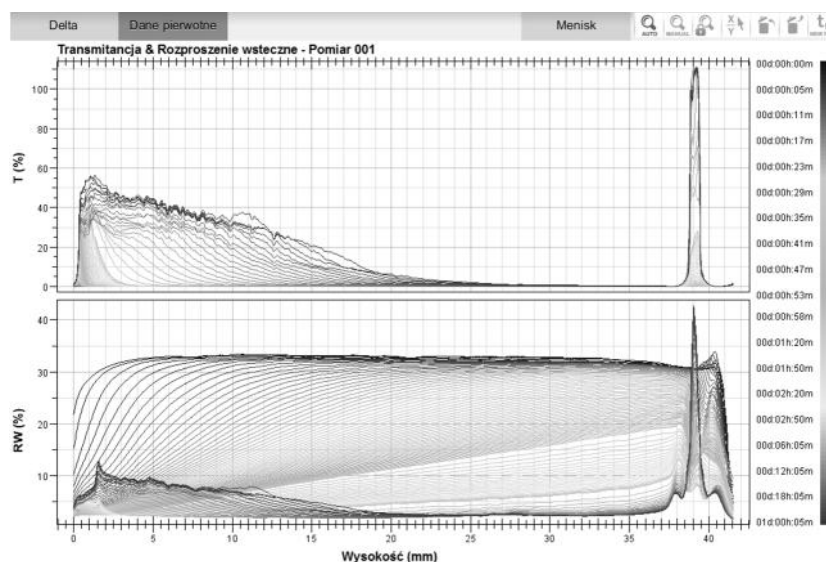


Fig. 9. Transmittance and back-scattering signal change in time versus height of the sample for 10ml addition of demulsifier for 10ml of 8% emulsion

Source: Author's

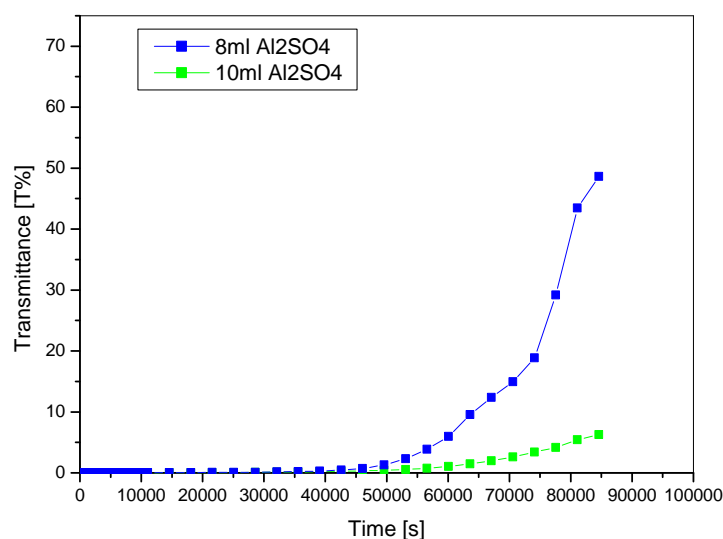


Fig. 10. Increment of transmittance for 8ml and 10ml addition of demulsifier for 10ml of 8% oil-in-water emulsion

Source: Author's

In Fig. 10 we presented the transmittance increment overtime for an addition of 8ml and 10ml demulsifier for 10ml of 8% emulsion. This parameter was obtained for a height of 15mm of the sample, since at 25mm of the sample the oil phase was present. As can be seen, the value varies for different amounts of additional demulsifiers. A bigger increment is observed for 8ml addition of emulsion breaker. It confirms our statement that this addition was optimal to separate phases in 8% emulsion.

### Summary and conclusions

The used cutting oils are considered to be hazardous waste that can be dangerous for the environment. One method of its disposal is separation of oil and water. Demulsification with aluminum sulfate appears to be a simple and efficient method of phase separation for the fluids. During analysis of process it is possible to notice the increment of transmittance signal varies over time. It is related to coalescence and phase migration during process. At the beginning the coalescence of droplets occurs, which can be observed by a rapid decrease in the back-scattering signal. Then the phase separates which can be noticed as the increment of transmittance



signals at the bottom of a measuring cell. The amount of 6ml aluminum sulfate with a concentration of 8g/l for 10ml of emulsion allowed the separation of phases in 4% emulsion completely in 24 hours, while the amount of 4ml of demulsifier needed 72hours to complete demulsification for this emulsion concentration. In the case of 8% emulsion, the most effective appeared to be 8ml additional aluminum sulfate for 10ml of emulsion. After the addition of 6ml the phase separation was not observed, while for 10ml addition the process was slower than for 8ml of demulsifier. Therefore, we concluded that the addition of 8ml of aluminum sulfate with a concentration of 8g/l for 10ml of 8% cutting oil emulsion is optimal dosage for phase separation.

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