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SEPARATION OF USED COOLANTS FROM HIGH-PRESSURE ALUMINIUM ALLOYS DIE-CASTING VIA TURBIDIMETRIC METHOD

Abstract: The growth of the automotive industry and increased efforts to reduce the environmental impact of transportation require the use of more and more aluminium components in the production of new cars. The process of high-pressure die casting of aluminium makes it possible to meet the goals, but it requires the use of coolants based on oil and wax emulsions that are difficult to dispose of. A method for demulsification of real wastewater samples from the high pressure die casting process was developed and evaluated. The optimal parameters for conducting the separation process were determined, and the changes occurring in the emulsion being separated were analysed.

Keywords: emulsions, coolants, demulsifiers, demulsification, separation methods

Introduction

Since 2023, there has been an upward trend in industrial production within the automotive industry [1]. Simultaneously, the tightening emission standards compel manufacturers to explore solutions that can adhere to increasingly stringent regulatory requirements. One such solution adopted by car manufacturers is the substitution of steel components with specialised aluminium alloys, facilitating a reduction in vehicle mass. As the utilisation of aluminium and its alloys surges, it becomes imperative to implement production processes capable of delivering products within designated timeframes while meeting rigorous quality standards. A prime example of such a process is high-pressure die casting of aluminium and its alloys. By utilising two-part moulding tools, this process facilitates the rapid production of high-quality products, a feat unattainable by other manufacturing techniques.

To facilitate the release of the finished product from the moulding tool and maintain it in proper technical condition, specialised cooling-lubricating agents are necessary. In this regard, aqueous solutions of oil or wax emulsions, typically ranging from 1 to 5 percent concentration, are commonly used. Unfortunately, once used, the coolant loses its properties and must be replaced with a new batch of fresh solution. Due to the high stability of spent emulsions and the difficulties in separating their constituent phases, their disposal

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processes are highly energy-intensive, directly impacting the economy of the entire production process. The high-pressure aluminium casting process, due to significantly higher investment costs than machining processes, results in significantly lower industrial availability. This situation has a direct impact on the limited cooperation of industry with the scientific community, which results in the low availability of scientific papers on the treatment of wastewater from the process of high-pressure casting of aluminium and its alloys, as opposed to papers devoted to the treatment of wastewater from machining processes.

The aim of the work performed was to develop effective methods for separating samples of actual wastewater from the casting process.

Numerous examples in the scientific and technical literature described the use of separation processes for treating spent cooling-lubricating emulsions [2-15]. In their review article, Yuying and et al. [2] divided demulsification methods into three groups based on the separation mechanism: physical, chemical, and biological methods. Regarding this work, it is important to mention chemical demulsification methods that used polymers, such as EO/PO block copolymers [3], PPQA@SiO_2 [4], or polyamidoamines as demulsifying agents [5]. Putatunda et al., in their review paper, presented several studies in which emulsions were separated by pH change, both by acidification and alkalisation [6-8]. Cerff et al. [9] focused on methods for treating oily water in their review article. The authors categorised the treatment methods according to the particle size of the dispersed oil. For particles smaller than 20 µm, they cited articles on methods such as coagulation, flocculation, air flotation, and the use of hydrocyclones and centrifuges [10-13]. Lazarevic and Stanisavljevic [14] discussed three levels of metalworking spent coolant treatment depending on the size and type of contaminants. They classified emulsion separation methods as secondary treatments, which included physical methods like heating, centrifugation, and filtration, as well as chemical methods based on the use of electrolytes such as acids, salts, or organic polyelectrolytes. Benito et al. [15] listed examples of emulsion separation using both physical methods like vacuum evaporation, ultrafiltration, and centrifugation, and chemical methods such as coagulation using $AlCl_3$ and $CaCl_2$. Liu et al. [16] conducted demulsification-based separation of spent coolant from machining processes using six inorganic salts: $CaCl_2$, $Fe(NO_3)_3$, $KAl(SO_4)_2$, $AlCl_3$, $Al_2(SO_4)_3$, and $FeCl_3$. Gierzatowicz and Pawlowski [17], in patent PL165104, described the method of demulsification of spent machining coolant employing iron salts Fe^{2+} and hydrogen peroxide. Rogos and Urbanski [18] investigated emulsion separation via the coagulation process utilising two inorganic salts: $Al_2SO_4 \cdot 18H_2O$, $FeSO_4 \cdot 7H_2O$, along with two cationic polyelectrolytes. Furthermore, Pacholski and Sek [19] conducted the separation of spent emulsion from machining processes using $Al_2(SO_4)_3$ and analysed the processes occurring in the separated system employing the Turbiscan Lab apparatus. In another study, Sek et al. [20] performed an analysis of the demulsification process using the Turbiscan Lab Expert apparatus.

As an alternative approach to treating similar wastewater with high COD and salinity, the method used by Kang et al. [21], using an aerobic membrane reactor based on dehydrated alum sludge, is presented.

This study aimed to investigate the feasibility of separating spent cooling-separating emulsions through demulsification. The objective of the demulsification studies was to determine the optimal parameters of the separation process for spent coolants originating from the aluminium casting process. To analyse the changes occurring during the

separation of the spent coolant, the turbidimetric method was used, enabling precise monitoring of the stability changes in the separated emulsion over time.

Experimental section

Materials

An averaged sample of used coolant was obtained from a facility manufacturing aluminium details using high-pressure die casting. For the demulsification process, a specialised demulsifier EXODEMUL MO (PCC EXOL S.A.) was utilised at a concentration of 1 %. This demulsifier is an aqueous solution containing surface-active compounds, solvents, and enhancing additives, including the sodium salt of di(2-ethylhexyl) sulfosuccinate and 2-(2-butoxyethoxy)ethanol.

Apparatus

The spent coolant emulsion was separated by mixing it with the demulsifier using a mechanical stirrer OS70-PRO (Chemland) equipped with a propeller tip (Fig. 1). The chemical oxygen demand (COD) in the water phase of the separated system was determined using a UV-VIS DR6000 spectrophotometer and compatible cuvette tests from the LCK series (Hach-Lange) [22].

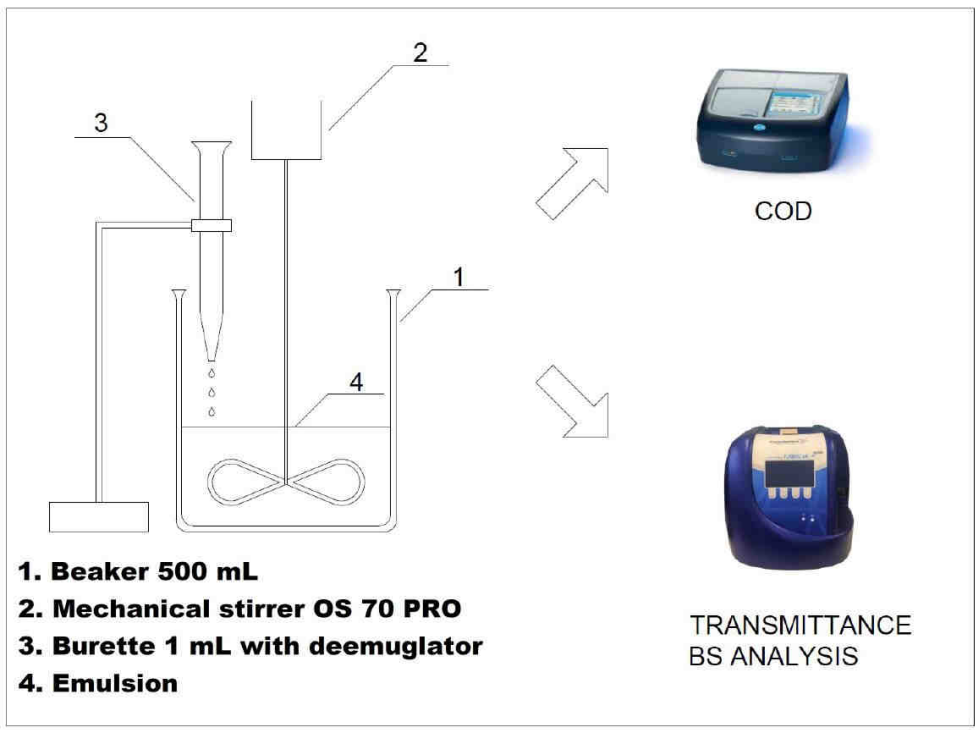

Fig. 1. Scheme of demulsification set-up

Optimisation studies of the demulsification process were conducted using the TurbiscanLab Expert device (Formulaction). This apparatus enables analysis of transmitted and backscattered light across the entire height of the sample under examination. The light source is a light-emitting diode that emits a focused beam of light in the near-infrared range (λ = 880 nm) [23]. The use of the turbidimetric method allows for the detection of subtle changes occurring in the system under study, which are often invisible to the naked eye. It also facilitates a meaningful comparison of changes between two different samples, greatly aiding in drawing accurate conclusions.

Research methodology

Preliminary studies demonstrated the feasibility of separating used coolant through demulsification using the EXODEMUL MO separating agent, concurrently reducing the chemical oxygen demand (COD) of the obtained water phase. Based on these findings, a decision was made to conduct optimisation studies of the emulsion separation process using the TurbiscanLab Expert device. These studies aimed to determine the influence of the separating agent's concentration (demulsifier), pH, stirring speed, and time on the emulsion destabilisation rate. A 100 mL sample of coolant was placed in a beaker. Subsequently, the system's pH was adjusted using 0.1M NaOH. The prepared coolant was then mixed with the demulsifier at the concentration being studied. The sample was stirred using a mechanical over-head stirrer at the tested rotational speed for a specified duration. After stirring, 20 mL of the sample was poured into a measuring vessel, which was immediately placed in the measuring cell of the apparatus, where the amount of light passing through the dispersion sample and backscattered from the sample was measured and recorded over time. Example graphs illustrating changes in transmittance and backscattering over time at different sample heights are provided in Figures 3 and 4.

The measurement of light passing through the sample and backscattered from the dispersion sample was conducted over an hour, with data points recorded every 25 seconds. The destabilisation rate of the coolant was determined based on the Turbiscan Stability Index (*TSI*), which is generated by the software algorithm of the device. The coefficient can be described by the following formula:

$$TSI(t) = \frac{1}{N_h} \sum_{t_i=1}^{t_{max}} \sum_{z_i=z_{min}}^{z_{max}} \left| BST\left(t_i, z_i\right) - BST\left(t_{i-1}, z_i\right) \right| \tag{1}$$

where t_{max} is the measurement point for which *TSI* is calculated, z_{min} and z_{max} are the lower and upper height limits, $N_h = (z_{max} - z_{min}) / \Delta h$ (changes in scanning height) is the number of height positions in the selected scan zone (Δh is a scanning height step), and *BST* is the considered signal (backscattering if $T < 0.2$ %, otherwise transmission) [22]. The higher the *TSI* value, the greater the observed changes in the stability of the examined system, indicating a more rapid destabilisation process. Once the index value is calculated, a series of samples can be graded and compared easily, accurately and objectively. The values are assigned a colour code that allows direct analysis and sample validation, thanks to the *TSI* scale, which links the values to corresponding visual observations. In the case of the A+ and A rankings, destabilisation is detected, but visual destabilisation is not observed (Fig. 2) [23].

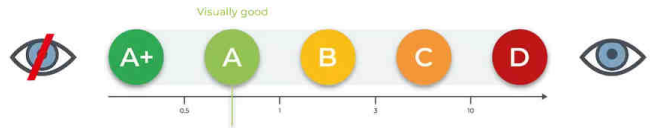

Fig. 2. *TSI* value stability ranking [23]

The study on the effect of the used demulsifier concentration on the separation rate of the coolant was conducted in the concentration range of 0.5 % - 3.5 %. Before measuring stability, the spent coolant with a pH of 5.5, along with the demulsifier, was mixed at a rotational speed of 1200 rpm for 10 min.

The study of the effect of separating agent concentration aimed to develop the most economically advantageous method for separating spent coolant.

The impact of pH on the destabilisation rate of the spent emulsion was examined in the range of 7.0 - 11.0. The raw coolant at a pH of 5.5, together with the demulsifier, was adjusted to the studied pH value using 0.1M NaOH and then mixed at a speed of 1200 rpm for 10 min. Examples of emulsion separation through acidification or alkalisation of samples can be found in the scientific literature. Altering the pH of the system changes the surface charge and reduces the zeta potential to zero, leading to destabilisation of the emulsion.

The influence of the mixing speed of the separated system on the destabilisation rate of the emulsion was investigated by mixing coolant samples at a pH of 10.0 with a 1 % addition of the demulsifier for 10 min at the following stirrer rotational speeds: 100, 300, 500, 700, 900, 1200 revolutions per min. The impact of mixing time on the destabilisation rate of the emulsion was determined based on the *TSI* parameter of emulsion samples at a pH of 10.0, mixed with a 1 % amount of demulsifier at a mixing speed of 500 rpm. The mixing times for the samples were 1, 5, 10, 15 min.

The COD of the water phase of the separated coolant was determined by placing 0.2 mL of the sample into the cuvette of the LCK 914 test (Hach-Lange). The sample was mineralised at a temperature of 170 °C for 15 min. After cooling, the COD was measured using the UV-VIS DR6000 spectrophotometer (Hach-Lange).

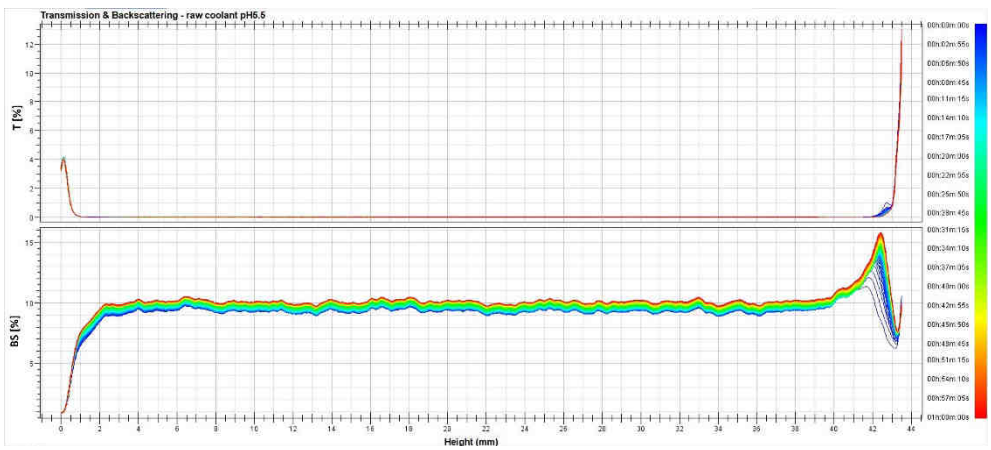

Fig. 3. Transmittance, *T* and backscattering *BS* for raw coolant

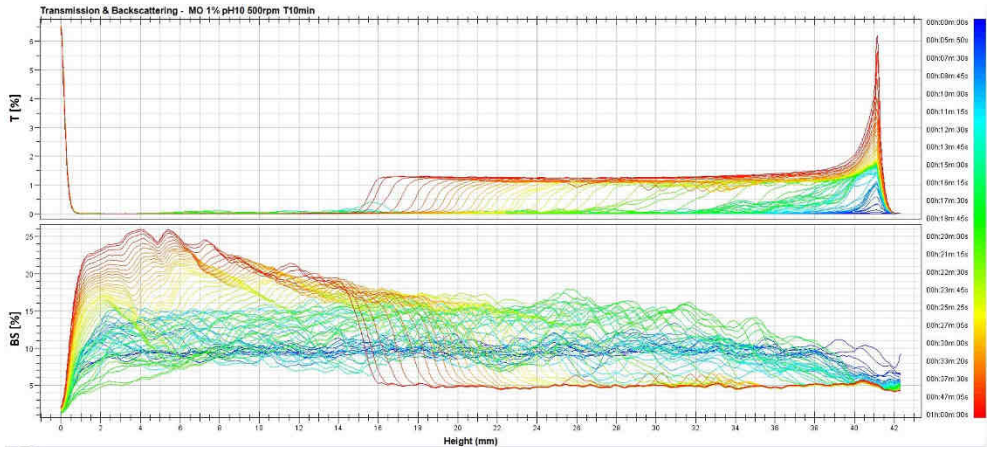

Fig. 4. Transmittance and backscattering for separated coolant (pH = 10.0, demulsifier concentration 1 %, stirrer speed 500 rpm, stirring time 10 min)

Research results and discussion

Preliminary research results on the separation of spent coolant demonstrated the feasibility of using the demulsification process to reduce the COD of the water phase of the spent emulsion. In the examined process, the concentration of the demulsifier was 1 %, the pH of the coolant was approximately 5.5, the stirrer speed was set to 500 rpm, and the mixing time was 5 min. The COD reduction amounted to 46 %, decreasing from a value of 14 600 mgO_2/dm^3 to 6700 mgO_2/dm^3. The continuation of more detailed research aimed at optimising the parameters of the process.

Effect of demulsifier concentration on coolant separation rate

Analysis of the impact of the amount of demulsifier revealed the following: One hour after the start of the measurement, the *TSI* stability coefficient reached its highest value for the sample with a 1% concentration of EXODEMUL MO, which was 19.1. Increasing the concentration of the separating agent led to a decrease in the *TSI* value compared to the sample containing 1 % demulsifier, down to a *TSI* value of 8.3 for a 3.5 % demulsifier concentration, indicating greater stability of the samples. Similarly, a lower demulsifier concentration (0.5 %) resulted in less effective dispersion destabilisation.

Table 1

TSI coefficient value depending on the concentration of the separation agent after 1 hour

Demulsifier concentration [%]	***TSI 1h* [-]**
0.0	1.0
0.5	13.7
1.0	19.1
1.5	11.9
2.0	10.0
2.5	12.8
3.0	10.6
3.5	8.3

However, compared to the *TSI* value for the raw coolant after one hour, which was 1, it is still significant. Analysing the destabilisation kinetics of the coolants (Fig. 5), a significant slowdown in the separation process (changes occurring in the samples) is evident just 30 min after starting the process.

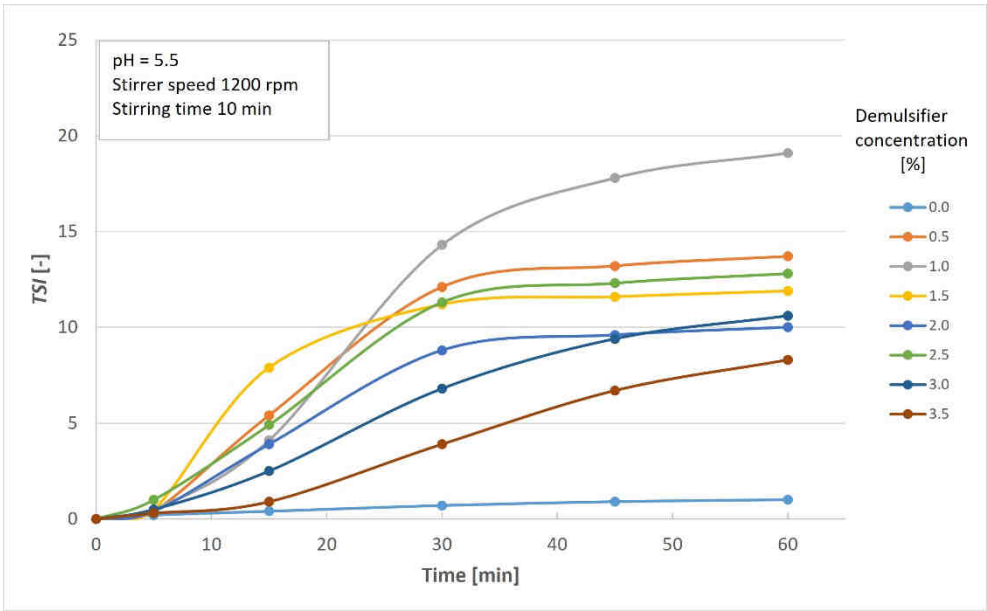

Fig. 5. Change in *TSI* over time as a function of the concentration of the demulsifier (pH = 5.5, stirrer speed 1200 rpm, stirring time 10 min)

Impact of pH on coolant separation rate

The influence of pH on the process was examined in the range of 7.0 - 11.0. *TSI* values recorded one hour after the measurement began and the kinetics of emulsion stability changes corresponding to the system's pH are presented in Table 2 and Figure 6.

Table 2

TSI coefficient value depending on the pH of the separated emulsion

pH [-]	***TSI 1h* [-]**
7.0	15.6
8.0	26.0
9.0	23.9
10.0	28.2
11.0	21.0

Based on the obtained results, a significant increase in *TSI* was observed for samples at pH 9.0 and 10.0, with values reaching 23.9 and 28.2, respectively, while a lower value was recorded for the sample with a pH above 10.0, which was 21.0. Consistently increasing *TSI* values were observed for samples with a pH above 7.0 throughout the measurement period,

unlike the sample at pH 7.0, where the change in *TSI* was only slight from 30 to 60 min. pH 10.0 was selected as optimal for the separation process and further research based on the gathered data.

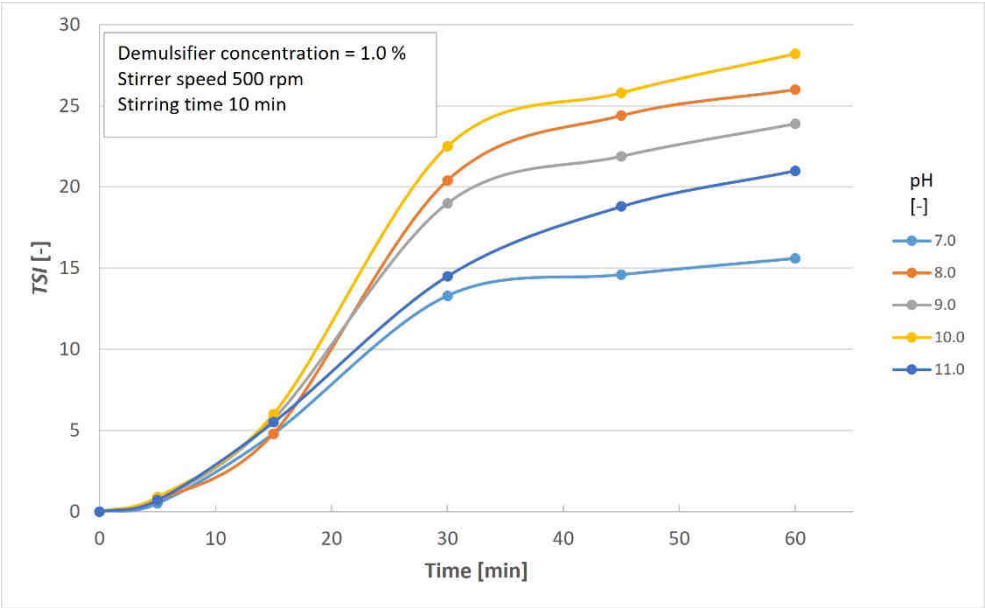

Fig. 6. Change in *TSI* coefficient over time depending on the pH of the system being separated (demulsifier concentration 1.0 %, stirrer speed 500 rpm, stirring time 10 min)

Impact of mixing speed on coolant separation rate

Table 3 and Figure 7 present *TSI* values and the kinetics of coolant destabilisation depending on the mixing speed of the separated system.

Table 3

TSI coefficient value depending on the emulsion stirring speed

Stirring speed [rpm]	***TSI 1h* [-]**
100	14.1
300	24.4
500	29.4
700	28.8
900	25.8
1200	19.1

The obtained *TSI* values indicate that setting the stirrer speeds in the range of 100-500 rpm allows for an increased rate of emulsion destabilisation compared to samples mixed at speeds of 700-1200 rpm in the first 15 min of the *TSI* measurement, which showed *TSI* values of 10-11. In contrast, for a stirrer speed of 700 rpm, a significant increase in the *TSI* value growth rate is observed from 15 to 60 min of measurement, increasing from 5.7 to 28.8 compared to samples mixed at speeds of 300 and 500 rpm. However, the final

TSI value for the sample mixed at 500 rpm is higher (29.4) than for the sample mixed at 700 rpm. The sample mixed at 500 rpm achieves the highest *TSI* values both after 15 min and an hour from the start of measurement; hence, this value was considered optimal for the demulsification process.

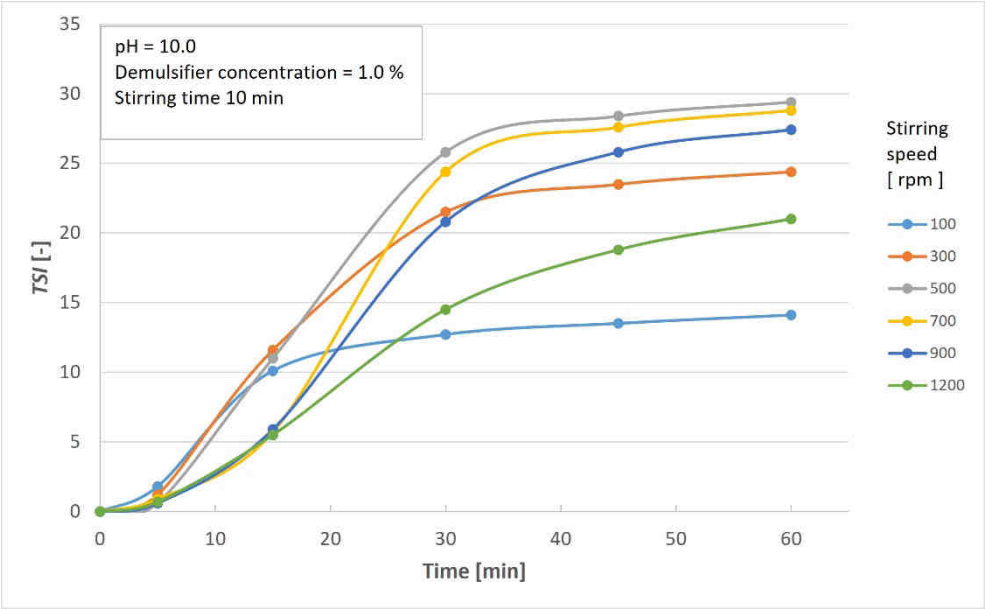

Fig. 7. Change in *TSI* coefficient over time depending on the stirrer speed (pH = 10.0 demulsifier concentration 1.0 %, stirring time 10 min)

Impact of mixing time on the coolant separation rate

The results of the investigation into the influence of mixing time on the rate of destabilisation are presented in Table 4 and illustrated in Figure 8.

Table 4

TSI coefficient value depending on the emulsion stirring time

Stirring time [min]	***TSI 1h* [-]**
1	17.5
5	28.9
10	29.4
15	27.7

It can be concluded that just after one min of mixing, it is possible to initiate the separation of the spent coolant (*TSI 1h* = 17.5). However, extending the mixing time to 5 min allows for nearly doubling the *TSI* parameter to *TSI 1h* = 28.9. Further extending the mixing time does not lead to significant changes in the progress of emulsion destabilisation. For all the tested coolant samples, the dynamics of separation significantly slow down after about 30 min from the start of measurement. The highest *TSI* values, both

after 30 min and one hour from the start of the measurement, were noted for the sample mixed for 10 min; therefore, this duration was chosen as the optimal parameter for conducting the separation process.

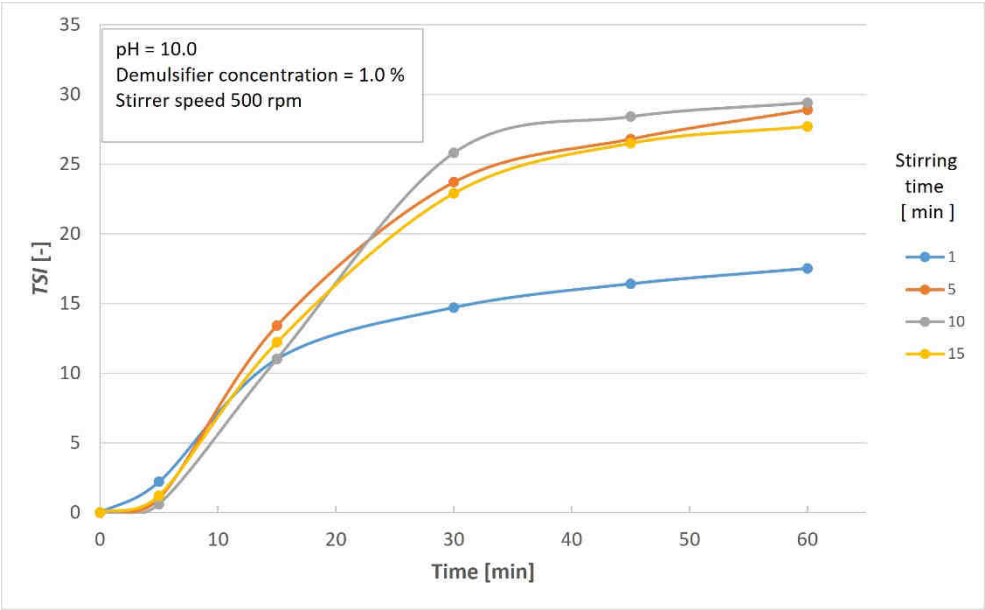

Fig. 8. Change in *TSI* coefficient over time depending on the stirring time of the separated emulsion (pH = 10.0, demulsifier concentration 1.0 %, stirrer speed 500 rpm)

Based on the investigation results presented above regarding the influence of individual process parameters on the separation ratio of spent coolant, the determined optimal parameters include a pH of 10.0, a demulsifier concentration of 1.0 %, a stirrer rotational speed of 500 rpm, and a mixing time of 10 min.

For the spent emulsion samples separated using the optimal process parameters, an analysis of COD reduction was conducted. The obtained value was 7100 mgO_2/dm^3 compared to 18 600 mgO_2/dm^3 in the sample of unseparated coolant, showing a COD decrease of 62 %. Optimising the separation process led to an increase in the efficiency of COD reduction from 46 % to 62 %, representing a 34 % improvement compared to the unoptimised process.

Summary

The preliminary studies demonstrated the feasibility of employing the demulsification process to separate spent coolants generated from the high-pressure die-casting process of aluminium. This method results in a water fraction with approximately 46 % lower COD compared to the untreated emulsion. Utilising the TurbiscanLab Expert (Formulaction) device facilitated precise monitoring of changes occurring in the separated emulsion over time. Subsequent optimisation studies explored the influence of demulsifier concentration, pH, stirring speed, and mixing time on the destabilisation rate of the spent coolant.

The studies revealed that the most unstable sample occurred at the demulsifier concentration of 1.0 %, with the highest *TSI 1h* value of 19.1. Increasing the demulsifier concentration within the range of 1.5 % - 3.0 % resulted in a decrease in the *TSI* value to 10.0 - 12.8, whereas further increasing the concentration to 3.5 % lowered the *TSI* to 8.3. Optimal demulsifier concentration facilitates the agglomeration of nonpolar oil or wax particles present in the emulsion into larger clusters, allowing them to settle freely at the bottom of the measuring vessel due to gravity. The reduced destabilisation observed in the separated emulsion with higher demulsifier concentration may be attributed to the steric hindrance caused by interacting demulsifier molecules, preventing oil particles from approaching each other and forming heavier aggregates. Higher *TSI* values indicate increased destabilisation of the examined emulsion, which in turn leads to better separation conditions and accelerates the separation process, thus significantly affecting the cost of treating spent coolants.

The study of the pH impact on emulsion destabilisation rate demonstrated a correlation between the pH increase and the changes in the *TSI* coefficient, a measure of dispersion stability. Increasing the pH from 7.0 to 10.0 resulted in an increase in *TSI* from 15.6 to 28.2, thereby reducing the stability of the separated system and enhancing the ratio of emulsion separation. However, when the pH was further increased to 11.0, a decrease in *TSI 1h* to 21 was observed. Samples with a pH higher than 8.0 exhibited significantly higher levels of destabilisation compared to the raw coolant at pH = 5.5, which recorded a *TSI* of 19.1.

Fig. 9. Comparison of raw emulsion (left) and separated coolant (right) (pH = 10, demulsifier concentration 1 %, stirrer speed 500 rpm, stirring time 10 min)

The adjustments made in stirring speed and mixing time alongside the demulsifier were intended to illustrate the threshold values necessary to initiate the separation process and identify optimal process parameters. The studies showed that stirrer rotations of 100 rpm were sufficient to initiate coolant separation. However, increasing the speed within the range of 500 rpm - 700 rpm resulted in notably higher *TSI* values after 60 min from the start of measurement (29.4 rpm for 500 rpm and 28.8 rpm for 700 rpm, and 14.1 rpm for 100 rpm). Further increasing the stirrer speed to 1200 rpm led to a decrease in *TSI* to 19.1,

possibly due to the disintegration of oil and wax aggregates forming in the emulsion, thus reducing their sedimentation rate at the bottom of the measurement cell.

Mixing time studies revealed that the initiation of separation occurred as early as 1 min into emulsion mixing (*TSI* = 17.5). However, extending the mixing time resulted in a significant increase in the *TSI* coefficient: 18.9 for 5 min, 29.4 for 10 min, and 27.7 for 15 min of mixing.

In all conducted analyses, the most rapid increase in the *TSI* coefficient was observed within the first 30 min of measurement. Extending the separation process duration to 60 min only led to a slight increase in the *TSI* coefficient, likely due to the faster settling of larger particles during the initial phase of separation.

Conclusion

The effectiveness of EXODEMUL MO as a separating agent in the demulsification process of spent cooling emulsions from the high-pressure die casting of aluminium and its alloys was successfully demonstrated. Optimisation studies were conducted to determine the optimal parameters for the demulsification process and to analyse changes in stability occurring in the separated coolant. The optimal process parameters identified are as follows: pH = 10.0, demulsifier concentration 1.0 %, stirrer rotational speed 500 rpm, and mixing time 10 min. Implementation of these optimal demulsification process parameters led to a notable increase in COD reduction from 46 % achieved during preliminary study to 62 % of the raw coolant value, as indicated by the analyses. The demulsification process significantly lowers the COD of the spent coolants, which, due to their high stability, pose a significant challenge in other disposal methods, including biological ones. The low concentration of the used separating agent and the rate of phase separation suggest demulsification as a viable alternative for the disposal of spent oil and wax emulsions.

The results obtained are consistent with those described in scientific papers. Rogos and Urabanski achieved a COD reduction of more than 60 % using polyelectrolytes to separate the spent emulsion [18]. In contrast, Sek and colleagues separated an emulsion with a concentration commonly used in the machining industry [20]. The separation rate they achieved was close to the estimated values and varied from 30 min to 60 min, depending on the concentration of the demulsifier used. In their study, Pacholski and Sek monitored changes in the emulsion being separated using a TurbiScan Lab apparatus [19]; however, in this case, the total coolant separation time ranged from 24 h to 72 h, depending on the parameters employed.

The demonstrated effectiveness of the applied demulsifier and the optimised parameters not only enhance the efficiency of demulsification but also provide a promising solution for managing high-stability emulsions. This approach offers a significant advancement in waste treatment technologies, potentially improving both environmental impact and operational efficiency in industrial processes.

Acknowledgements

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