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Screening of Gel Formation Methods in Paraffin Based Systems

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Executive Summary

The Savannah River National Laboratory (SRNL) has evaluated gel formation in kerosene using a lecithin-based system, the aluminum soap of naphthenic and palmitic acid or derivatives, and an acrylamide copolymerization. Some gelling was observed in the lecithin system, but not sufficient gelling to meet the customer's needs. The napthenic systems provided a good degree of gelling yet required a larger wt.% than the customer desires. The acrylamide copolymerization gels easily in aqueous systems yet does not extend to an organic system.

Introduction

The PUREX process has been the work horse for the separation of plutonium since the early 1950's. The chemistry of the process was applied for patent in 1947. Historically, the PUREX process involves the dissolution of irradiated fuel in nitric acid followed by mixing with an organic solvent (30% tributyl phosphate (TBP) in Kerosene). The first cycle of a flowsheet can achieve > 99.8 % U and Pu in the organic phase. Valence adjustment of the Pu allows for stripping the Pu to a new solution leaving the U in the organic phase.

The longevity of PUREX lies in its track record as an efficient and robust separation flowsheet. Radiation and acid attack slowly decompose TBP into lower alkylphosophoric acids which decreases the efficiency through increased losses of fissile materials to the aqueous streams. Operationally, the alklyphosphoric acid is readily removed by washing the TBP solution successively with Na_2CO_3 prior to reacidification with dilute nitric acid.

Many decades of research have provided much working knowledge on maintaining the efficiency of the process and proving the robustness in the technology. The process could be interrupted through means of degradation of the solvent, but it is expected and planned that limited degradation will occur during normal operation. Rendering the organic unusable could interfere with the process until new TBP/Kerosene are obtained. However, rendering the solvent unusable inside the solvent extraction equipment in the reprocessing plant could lead to many months of delays or a total loss to the plant.

SRNL proposed to explore rendering the organic phase useless in situ by forming a solid gel inside a PUREX type plant. Work presented herein has evaluated the gel formation in kerosene using a lecithin-based system, the aluminum soap of naphthenic and palmitic acid or derivatives, and an acrylamide copolymerization.

Assumptions

- Adulterate will be delivered into the organic feed
- If an initiating agent are needed, they are present in sufficient quantities due to the processing of irradiated fuel
- Gelled organic phase does not mix with aqueous phase which could then pass through system

Experimental/Discussion

The initial phase has focused on literature and fundamental chemistry to identify potential gelling agents. Three potential gelation systems have been selected for evaluation: 1) acrylamide polymerization, 2) lecithin organosols, and 3) an aluminum based fatty acid soap. The selected agents have been evaluated on a small scale in a pure paraffin system using kerosene.

Acrylamide Copolymerization

Gels can be obtained through free-radical crosslinking copolymerization of acrylamide and N,N'-methylene-bisacrylamide (MBAM).[1] Following the experimental ratio for reagents from the Stern email[2], experiments were scaled from 200 mL to 4 mL for 4 M HNO_3 and applied to both 4 M HNO_3 and kerosene. The large-scale ratio was 10:1:1 mass ratio for acrylamide, MBAM, and sodium persulfate respectively. After adding reagents to the nitric acid and kerosene, the solutions were heated to 40 °C for 30 minutes. The reagents dissolved immediately in the nitric acid but did not dissolve at all in the kerosene by visual inspection. After heating, the vials were left open to cool and checked later in the day to find a gel formed in the nitric acid (

Figure 1) and no gel formed in the kerosene (

Figure 2). At 6 wt% adulterant in the nitric acid system the gel does form however an estimated 20% of the acid does not gel (Figure 1). Since the gel agents did not appear to dissolve in the kerosene and no gel formed, no attempt was made to determine if any of the gel agents had dissolved.

Figure 1: Gel formed with Acrylamide/MBAM in 4 M HNO₃

Figure 2: Acrylamide/MBAM in Kerosene does not dissolve and does not gel.

Lecithin

The zwitterionic phospholipid, lecithin, can self-assemble into reverse micelles in organic solvents forming a lecithin organogel.[3] Salts of multivalent cations have been shown to greatly increase the viscosity of a lecithin organogel.[3] Using methods described by Lee et al.[3], L-α-Phosphatidylcholine (lecithin from soybean) was used along with calcium (Ca^{2+}) to transform kerosene to a gel.

The two basic prep methods presented by Lee et al. were modified for the present work. The first method dissolves the lecithin and calcium chloride in methanol, dries the solution in a furnace, and dissolves the residue with organic solvent at the optimum lecithin and Ca^{2+} concentrations of 20 mM and 14 mM respectively prior to heating to 60 °C. In the second method, a concentrated solution of lecithin/Ca^{2+} is prepared in ethanol and added to the kerosene to achieve the same 20 mM/14 mM concentration.

Since the first method requires an additional undesired step to heat the solvent to 60 °C, the drying of the methanol step was eliminated thus adding the methanol/lecithin/Ca^{2+} *solution directly to the kerosene. This method modification resulted in drops of a "gel" formed in the solution which did not thicken when left overnight at room temperature. The lecithin and* $CaCl_2$ *required ~2 mL of ethanol to dissolve enough to make a targeted 20 mM/14 mM concentration. Due to the unexpected increased volume required for dissolution, when added to the kerosene, the real concentration becomes ~ 10 mM and 7 mM respectively for the lecithin and* Ca^{2+}*. The dilution hindered the gel formation, providing only a few gel drops as observed in Figure 3. The lecithin/*Ca^{2+} *was next added dry with stirring directly to the kerosene in and attempt to circumvent the methanol and heating steps altogether. The reagents did not dissolve and thus did not form a gel as observed in the vial labeled Test 3 in*

Figure 4.

The second method presented in the literature claims to be a room temperature reaction in the formation of the gel when using a previously prepared lecithin/Ca^{2+} solution. Inconsistencies were observed with the concentrations reported in the literature for the stock solution preparation. The lecithin and $CaCl_2$ were not soluble to the 620 mM and 220 mM concentrations respectively stated in the open literature. The authors then added enough stock solution to achieve 40 mM and 14 mM concentrations for the lecithin and Ca^{2+}. Due to the lower solubility, a stock solution at 62 mM lecithin and 22 mM Ca^{2+} was prepared. Even though the solids did not completely dissolve, 3 mL of stock solution was added to 5 mL kerosene to achieve [lecithin] and [Ca^{2+}] in dry kerosene at 40 mM and 14mM respectively. A loose gel appeared to form but this gel dissolved within 36 hours, thus not achieving the goal for this program. No additional work was conducted using the lecithin.

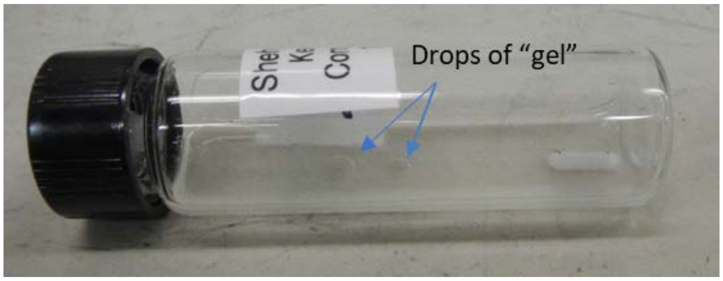

Figure 3: Addition of methanol-based solution of lecithin and calcium chloride

Figure 4: Test 3 showing the undissolved reagents as compared to #2 (also shown in Figure 3).

Napthenic

Thickening agents for fuels have been of interest for at least 100 years. One of the most widely known thickening agents is Napalm.[4] This name was originally coined in the 1940s from the production of an aluminum soap from naphthenic and palmitic acids though now the term could be used for any aluminum soap based on a fatty acid. In fact, soon after the term was coined, it was found that gelling quality was based on high contents of lauric and not palmitic acid.

This work selected the formulation from the Napalm report where an aluminum soap of a mixture of dodecanoic, oleic, and naphthenic acids is prepared through precipitation of the aluminum soap.[4] The aluminum soap is prepared by dissolving the fatty acids in 25% sodium hydroxide and precipitating by adding a solution of aluminum(III) sulfate ($Al_2(SO_4)_3$). The resulting precipitate was wet and clumpy. This product was placed in a muffle furnace for ~4 hours to dry before use. Adding soap at 5 wt% to kerosene using only a magnetic stir bar did not result in visible gelling of the system. When ground to a fine powder, the 5 wt% addition *demonstrated some gelling. However, when incorporating the aluminum soap at 20 wt% with a tissue homogenizer, a gel will form as shown in Figure 5: Al soap of naphthenic, oleic, and dodecanoic acids prepared by methods presented in Feiser et. al. Material has been dried in a muffle furnace and stored under flowing argon.*

. In 4 mL of kerosene this gel sets to soft gel consistency as shown in Figure 5: Al soap of naphthenic, oleic, and dodecanoic acids prepared by methods presented in Feiser et. al. Material has been dried in a muffle furnace and stored under flowing argon.

. The gel could be scooped out of the vial without slumping off a spatula.

It is well documented that aluminum soap is hydroscopic and military use states once the container is open it need to be added to the organic in a timely manner. To dry the lab made aluminum soap, it was placed under a dry argon purge for 3 days prior to additional use. Repeating the previous test matrix at 5, 10, and 20 wt% and mixing with a tissue homogenizer, gels were produced at all concentrations, Figure 7Figure 9. As can be seen, the gel quantity increased with an increase in the wt% of the aluminum soap added. This time, even at the 20 wt% target, the gel did not completely set. In all cases, two "phases" were observed within 10 minutes with a gel appearing same day (~5 hours).

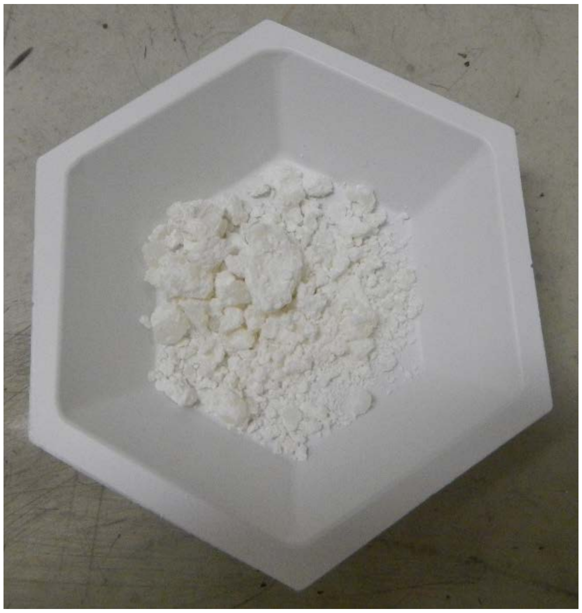

Figure 5: Al soap of naphthenic, oleic, and dodecanoic acids prepared by methods presented in Feiser et. al. Material has been dried in a muffle furnace and stored under flowing argon.

Figure 6: Aluminum soap added as prepared to kerosene at 20 wt%

Figure 7: Degassed aluminum soap added to kerosene at 5 wt%

Figure 8: Degassed aluminum soap added to kerosene at 10 wt%

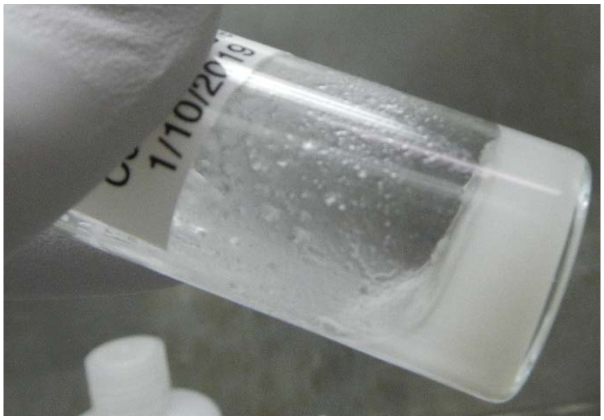

Figure 9: Degassed aluminum soap added to kerosene at 20 wt%

Conclusion

The deliverable for Phase 1 testing of gel forming adulterants is the documentation of details for the use of adulterates evaluated through the proposed test matrix.

The acrylamide copolymerization can be quickly ruled out as a viable option since the reagents are not soluble in kerosene. A similar polymerizing system that is soluble in an organic fuel could exist but was not identified in the literature prior to the start of the presented tests.

In the creation of lecithin organogels, Lee et. al. document the successful production of gels in kerosene through various methods. Each method has drawbacks with the two main drawbacks of delivery of adulterants in a liquid form and prep time with heating to form a dry residue that is reactive toward kerosene. The ethanol-based room temperature method could not be reproduced in this lab using the experimental details in Lee et. al. In the room temperature method, the lecithin would be added to the kerosene at ~4 wt% theoretically. For this system to be a viable option, the active reagent prepared in the methanol dissolution/drying method would need to be prepared in bulk for delivery into the kerosene.

Of the three gel forming systems screened in this work, only the napalm-based system was successful at forming a gel in kerosene. When using the precipitated form of the aluminum soap from the naphthenic, oleic and dodecanoic acids, a gel was shown to form by at a much more fluid consistency and at a higher wt% adulterant use than preferred. It is possible that some of the other formulations described in the literature could provide more consistent results and a firmer gel product as it would have known pedigree in production method and exact optimization of organic acid blend.

References

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