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# Sulphuric Acid as Neutralization Agent for the Removal of Caesium in the Production Process of a Commodity Polyether-Polyol

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**ABSTRACT:** The aim of this work was the optimization of the neutralization process to remove the catalyst from a polyether polyol. Some parameters were studied: water content, dehydration curve conditions, the acid concentration of the neutralization solution, and temperature. The final cesium content was kept under the specified value. However, the final value of polyol acidity was higher than that of the commercial specification for these kinds of polyol.

## 1. INTRODUCTION

Polyether polyols are usually produced according to the same basic process, namely by reaction, in the presence of a basic alkoxylation catalyst, of an initiator compound having active hydrogen atoms with alkylene oxides, such as ethylene oxide or especially propylene oxide. A great research effort to develop a new initiator or a new finishing process to reduce unsaturation has been done by the petrochemical companies involved in polyol and polyurethane production. Most of this research has been focused on the use of cesium hydroxide instead of potassium hydroxide and is covered under patents due to its industrial interest.[1−5] Cesium hydroxide is an excellent alternative catalyst for polyol production, since it decreases the synthesis time and unsaturation content of polyols.[6,7] In all cases, after completion of epoxidation, cations have to be removed from the polyol (final concentration must be lower than 5 ppm), because traces of base lead to unwanted secondary reactions in the subsequent polyurethane production.[8] In cesium removal, recovery of cation is also critical due to the high cost of the product and so that it is necessary to find a suitable method to recover and reuse the alkali metal catalyst.[9]

Although the amount of catalyst employed is not actually large (1% of the final polyol weight), the high price of cesium hydroxide if is not recovered, makes the process economically unfeasible. Regarding the elimination and recovery of the alkaline metal catalysts from polyols, several scientific works can be found in the literature.[10−14]

Tsutsui et al.[12] reported a process in which a crude polyalkylene polyol containing the catalyst was neutralized with a mineral acid. An aqueous solution layer containing an alkali metal salt was brought into contact with an anion exchange resin to adsorb mineral acid anion; the alkali metal compound catalyst was recovered.

Pérez-Collado et al.[14] studied the removal of cesium from polyether polyols by ion exchange. Thus, ion exchange process, equilibrium, kinetics, regeneration, and final purification of cesium were reported. The cesium final level in polyol was well under the commercial specifications required for this kind of products.

Ma et al.[15] reported the purification of polyether polyols made by double metal cyanide catalysis. The removal of residual double metal cyanide in the polyols was made by adsorption and precipitation−filtration. The residual concentration of the zinc and cobalt ions was measured by ICP. Compared with precipitation−filtration, the method of adsorption was more practical and efficient for the purification of the polyols.

In our previous work,[16] the recovery of cesium hydroxide from crude polyether polyols was carried out. Experiments were limited to the use of a 6000 $M_W$ with an EO tip grade polyol (polyol F-2831). Parameters such as water content, temperature, time, and neutralization agent amount (sulphuric acid) were optimized, taking into account the final cesium content, acidity of polyol, and particle size in order to recover the neutralized catalyst by filtration. An optimum particle size of cesium sulphate crystals was obtained when water content in the range 2−3 wt % was used. The cesium content was kept under specification if the neutralization temperature was maintained at 110 °C. Finally, although the final particle size allowed us to obtain a good filtration process, meeting the specification for cesium content in the polyol, the acidity of the polyol did not allow us to obtain a final product with all the parameters under specification, suggesting the necessity to find a new process to remove the catalyst.

The aim of this current work was to find an optimum process to recover the catalyst (cesium hydroxide) on the polyol production process. In this case, a new polyol was used (molecular weight of 3500). Parameters such as water content, dehydration temperature and time, sulphuric acid amount, and neutralization temperature were optimized.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The experiments were limited to the use of a 3500 $M_w$ polyol cofeed by PO/EO (polyol F-4811),

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synthesised as described elsewhere[9] with cesium hydroxide as catalyst.

Sulphuric acid 95–98% (PANREAC PRS-codex grade, Barcelona) was used as neutralization agent.

**2.2. Characterization.** Cesium content was measured by atomic emission in a Varian Spectra AA 220 FS atomic absorption spectrometer. The polyol samples were diluted with methanol (1:5 by weight) in order to reduce their viscosity.

The water content of polyol was determined by the Karl Fischer method in an automatic TITRINO KF with stirring and suck system TI STAND 703 according to ASTM D 4672-87. Water and iodine are consumed in a 1:1 ratio in the above reaction. The amount of water present in the sample is calculated voltametrically based on the concentration of iodine in the Karl Fischer titrating reagent (i.e., titer) and the amount of Karl Fischer reagent consumed in the titration. Hydranal Composite 5 (Fluka, Germany) and methanol according to Karl Fischer (Panreac, Spain) were used as reagents.

Acidity was measured by automatic titration in a METROHM 721 Net Titrino according to ASTM D 4662-87. To determine the acidity, a weighted sample of polyol is dissolved in a 50% mixture of toluene and ethanol and titrated with an ethanolic KOH solution.

Crystal size distribution was determined by using a MASTERSIZER 2000 instrument (Malvern), which was based on the technical “low angle laser light scattering” (LALLS). The entire 0.02–2000 $\mu$m measurement range is accessed using a single-lens system.

Particles morphology was determined from micrographs taken with a LEICA LEITZ-DMRXP scanning electron microscope using a sample magnification of 100.

## 3. RESULTS AND DISCUSSION

**3.1. Influence of the Water Content.** The optimization of the water content on the polyol neutralization is the most important factor to obtain crystals with a suitable size to be filtered.[16] In our previous work,[16] the amount of water added with the acid used to neutralize a 6000 $M_w$ polyol (F-2831) was optimized. In this case, the optimization of the purification process of a glycerol based polyol with 3500 $M_w$ will be the goal of the work. The first stage was to establish the optimal amount of water that was to accompany the stoichiometric amount of acid. For that, 150 g of polyol was placed in eight hermetically sealed vessels, and the temperature was kept under the constant value of 70 °C. Initially, the stoichiometric amount of $H_2SO_4$ to form cesium sulphate was added, calculated on the basis of the cesium hydroxide added as catalyst. The contact time between the acid solution and the polyol was 5 h, a time considered long enough to get a proper crystallization of the cesium sulphate crystals. After that period, the crystals size and the cesium content on the polyol were measured. Results are shown in Table 1.

It is considered that the filtration process at industrial scale can only work properly when the crystal size is greater than 1 $\mu$m. Two parameters were measured after the contacting period: the average particle size and the cesium content of polyol once filtrated. It is possible to confirm in Table 1 how when the amount of water added with the acid was ≤1 wt %, the crystal size was less than 1 $\mu$m: a size not suitable for being filtered. The solution presented a cloudy aspect, and the cesium content was very high for water contents of 0.2 and 0.4 wt %.

However, for water contents higher than 1 wt %, a clear solution with well-formed crystals was obtained. The crystals formed had a size large enough for filtration when an amount of water in the range of 3–4 wt % was used. The cesium content was not under specification (≤10 ppm), but in order to choose optimum water content, a value of around 3 wt % was selected as the target point to adjust the water addition to obtain a crystal size suitable for filtration. This amount of water will be the starting point for the optimization of the crystallization process.

Table 1. Optimization of Water Content in the Catalyst Neutralization at 70 °C during 5 h

| experiment | $H_2O$ (wt %) | aspect | dp(0.5) num ($\mu$m) | Cs (ppm) |
|---|---|---|---|---|
| 1 | 0.2 | cloudy | 0.19 | over[a] |
| 2 | 0.4 | cloudy | 0.19 | over |
| 3 | 0.6 | cloudy | 0.20 | 11.8 |
| 4 | 1 | cloudy | 0.20 | 10.6 |
| 5 | 1.5 | clear | 2.48 | 27.2 |
| 6 | 2 | clear | 3.83 | 25.6 |
| 7 | 3 | clear | 7.10 | 38.2 |
| 8 | 4 | clear | 4.78 | 62.3 |

[a] Value over the range of calibration.

In Table 1, it is possible to observe a crystal size less than 5 $\mu$m and a higher cesium content on the polyol (62.3 ppm), when 4 wt % of water was used. The cesium sulphate crystals can be to some extent solubilised when the amount of water used is higher than 3 wt %,[16] increasing the cesium content in the final polyol.

**3.2. Optimization of the Dehydration Curve.** With the latter results, it should be possible to optimize the dehydration curve in order to obtain crystals with a suitable size in order to be filtered and the cesium content specified. Four experiments with different initial amounts of water (in the optimum range, 1.5–3 wt %, to obtain high crystal sizes) and sulphuric acid contents were performed. A dehydration profile with two steps was employed to accomplish the crystallization: the first one, the so-called the neutralization step, with a duration of 90 min, was developed at atmospheric pressure and 110 °C; the second one, a dehydration–crystallization with a duration of 60 min, was carried out at a pressure below 10 mbar and 110 °C. In this second step, water was removed from the polyol and cesium sulphate crystals were formed. The final crystal size and cesium content of the polyol for the different experiments are shown in Table 2.

Table 2. Crystal Size and Cesium Content by Varying the Water and Sulphuric Acid Content

| $H_2O$ (wt %) | $H_2SO_4$ (wt %) | dp(0.5) vol ($\mu$m) | dp(0.5) num ($\mu$m) | Cs (ppm) |
|---|---|---|---|---|
| 1.5 | stoichiometric | 402.1 | 6.21 | 62.4 |
| 2 | stoichiometric | 17.4 | 0.99 | over[a] |
| 3 | stoichiometric | 155.2 | 4.07 | over |
| 3 | 5% in excess | 196.7 | 3.61 | over |

[a] Value over the range of calibration.

The largest crystal size in number (6.2 $\mu$m) was obtained by using 1.5 wt % of water and the stoichiometric amount of sulphuric acid. However, this size is not the best to be filtered. The particle diameter in volume (402.1 $\mu$m) revealed that the major part of particles were really small. In addition, in these neutralization conditions, the final cesium content remained somewhat high (62.4 ppm), largely out of specification.

Finally, the employment of a slight excess of sulphuric acid for a water content of 3 wt % did not improve the results, obtaining once again small particles and a cesium content out of specification.

In order to follow the evolution of the crystal growth with time to see if there exists a relation between water content and crystal formation, an experiment with a water content of 10 wt % and the stoichiometric amount of $H_2SO_4$ was performed. The neutralization was extended for 6 h at 750 mbar, taking samples each 15 min. The second step for the complete dehydration and crystallization was maintained during 2 h at pressures below 10 mbar. The evolution of humidity and crystal size during the experiment is depicted in Figure 1. While the humidity of polyol decreases continuously with time, the crystal size increases just during the first 60 min and after that remains stable, even at the vacuum period (after 360 min). The crystal size after the dehydration curve is relatively small and not suitable for a quick filtration (<4 μm), and additionally, the final polyol had high cesium content (143 ppm).

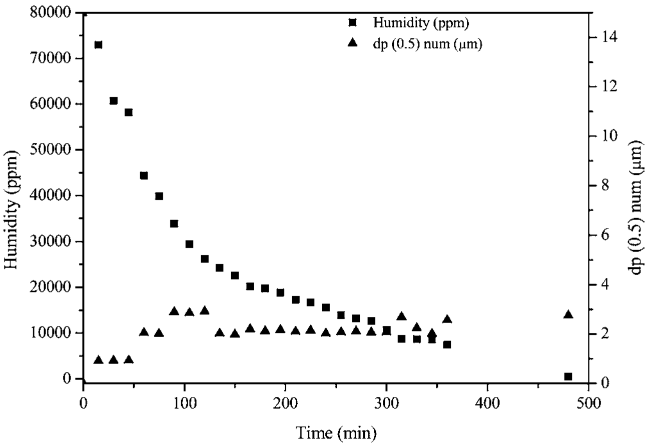

**Figure 1.** Evolution of humidity and crystal size with time.

In order to obtain a polyol of certain specifications, it is necessary to obtain not only large crystal sizes but also cesium contents lower than 10 ppm. With an initial water content of 0.6 and 1 wt %, it was possible to get a really low cesium content (Table 1). Two new experiments were carried out by using these two values for the content of water in the neutralization. In this case, a two steps neutralization and dehydration−crystallization protocol were performed at 110 °C. The first step was carried out at 700 mbar during 120 min and the second one at pressures below 10 mbar and during 60 min. Samples were taken each 40 min. Results are shown in Table 3.

It was observed how the final cesium content was lower when a water content of 0.6 wt % was used. However, in these conditions, the crystal size was suitable at 40 min (4.9 μm), decreasing strongly with the time. In addition, this value of water content did not allow us to obtain a final cesium content under specification. Therefore, probably the theoretically stoichiometric amount of acid used for the neutralization was not well calculated or the effectivity is not complete and obviously this point deserved more attention.

### 3.3. Influence of the $H_2SO_4$ Amount on the Polyol Quality.

In all the previous experiments the cesium is never completely removed in the crystallization−filtration process. This means that there is a small part that is not forming particles retainable in the filtration process. We had a suspicion about the possibility of removing all the cesium using a certain excess of $H_2SO_4$. Hence, a set of experiments to see the influence of using a certain excess of sulphuric acid on the crystal size and cesium removal was carried out. Five experiments, varying the sulphuric acid added for neutralization in the range from the stoichiometric amount to 100% in excess, were carried out. During the neutralization step, pressure and temperature were maintained at 700 mbar and 110 °C, respectively, and two samples were taken at 40 and 100 min (Figure 2). The dehydration−crystallization was carried out at the same temperature, during 60 min and a pressure below 10 mbar. In all cases, water was maintained in a weight ratio of 1/1 with respect to the sulphuric acid added. This means that the amount of water added was in the range of 0.37−0.74 wt % of polyol weight.

**Table 3. Crystal Size and Cesium Content by Varying the Water (0.6 and 1 wt %) and Sulphuric Acid Contents**

| $H_2O$ (wt %) | $H_2SO_4$ | time (min) | dp(0.5) num (μm) | Cs (ppm) |
|---|---|---|---|---|
| 1 | stoichiometric | 40 | 0.63 | |
| 1 | stoichiometric | 80 | 1.22 | |
| 1 | stoichiometric | 120 | 1.29 | |
| 1 | stoichiometric | 180 | 2.39 | 104 |
| 0.6 | 1/1 $H_2SO_4$/ $H_2O$ | 40 | 4.90 | |
| 0.6 | 1/1 $H_2SO_4$/ $H_2O$ | 80 | 1.31 | |
| 0.6 | 1/1 $H_2SO_4$/ $H_2O$ | 120 | 1.32 | |
| 0.6 | 1/1 $H_2SO_4$/ $H_2O$ | 180 | 1.56 | 37.6 |

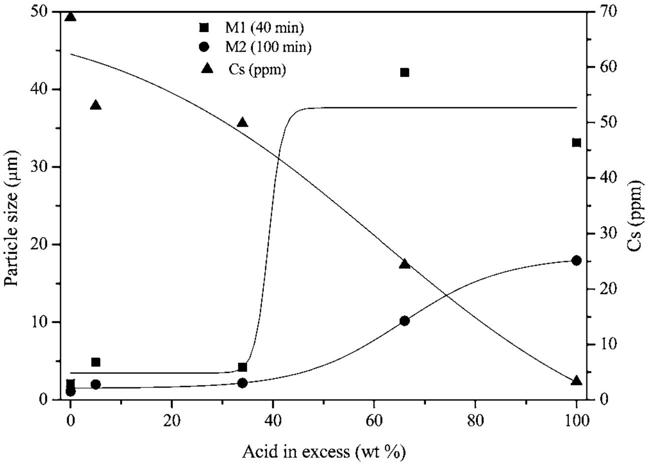

**Figure 2.** Cesium content and particle size for different acid amounts.

Figure 2 shows the cesium content and the crystal size (at 40 and 100 min of the neutralization process) for the different amounts of acid assayed. Cesium content decreased with an increase of the sulphuric acid excess, with an excess of 100% with respect to the stoichiometric amount being the right amount to get the cesium content under the specification value (<10 ppm). Besides, the final particle size (M2 at 100 min) obtained allowed crystals to be filtered properly. It is worthy to observe how the particle size decreased during the neutralization process (particle size at 100 min lower than at 40 min).

To check the robustness of our process and in order to avoid the crystals decreasing, the experiment using 100% of sulphuric acid excess was repeated. In this case, after 40 min, polyol was filtered in order to remove the crystals of cesium sulphate and then, high vacuum was applied, in order to remove the humidity. A crystal size of 33.5 $\mu$m (for crystals obtained at 40 min) and not detectable content of cesium were obtained, so that we had a robust and predictable crystallization procedure. The cesium content of the polyol was into the specification, and the filtration was really quick and efficient.

In our previous works using the stoichiometric amount of sulphuric acid, it was possible to get a complete removal of cesium from a 6000 $M_w$ polyol (F-2831).[9,16] With the 3500 $M_w$ polyol, double the stoichiometric amount of sulphuric acid to form $Cs_2SO_4$ is necessary. This would mean that probably $CsHSO_4$ is being formed and that only the first proton of the sulphuric acid is strong enough to catch the Cs that is ion-paired to the end of the polyol chain. Hence, it was necessary to confirm that the salt obtained in the neutralization process was cesium hydrogen sulphate. Figure 3 shows the X-ray diffractogram for crystals obtained after neutralization. The obtained peak position and subsequent *d*-spacing confirm the orthorhombic crystal structure of cesium hydrogen sulphate with two main peaks at 3.64 and 3.54 Å. However, the peaks for $Cs_2SO_4$ should appear at 3.29 and 3.15 Å, confirming that the diffractogram corresponds to $Cs_2HSO_4$.

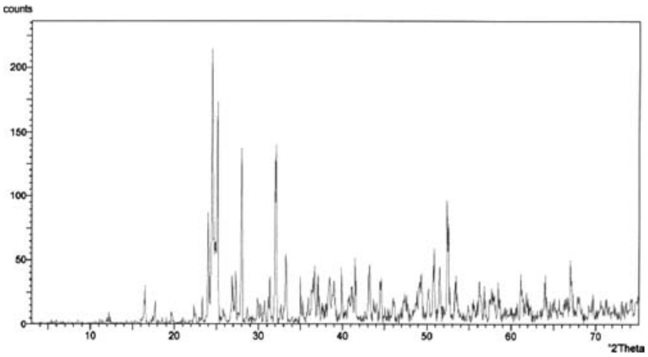

**Figure 3.** X- ray diffractogram of cesium hydrogen sulphate salt.

The morphology of the salt crystals compared with crystals of cesium sulphate (obtained from the neutralization of the 6000 $M_w$ polyol) is shown in Figure 4. Crystals of cesium hydrogen sulphate were of higher size than crystals of cesium sulphate. The crystal shape was notably different, although in both cases the filtration was accomplished satisfactorily.

So different behaviour of both polyols with respect to sulphuric acid neutralization should have an explanation based on their chemical differences. While F-2831 is an EO tip grade polyol finished in primary hydroxyl group, F-4811 is a cofeed PO/EO polyol, finished mainly with secondary hydroxyl groups. Taking into account that only the strongest of the sulphuric acid hydrogens is active enough for neutralizing the F-4811, it can be concluded that the ionic linkage of the Cs with the secondary hydroxyl group of the polyol is stronger than that with the primary hydroxyl group. In terms of acidity, the second proton of sulphuric acid is not strong enough to displace the Cs ion transforming the secondary alkoxide formed at the end of the polyol chain into the alcohol form.

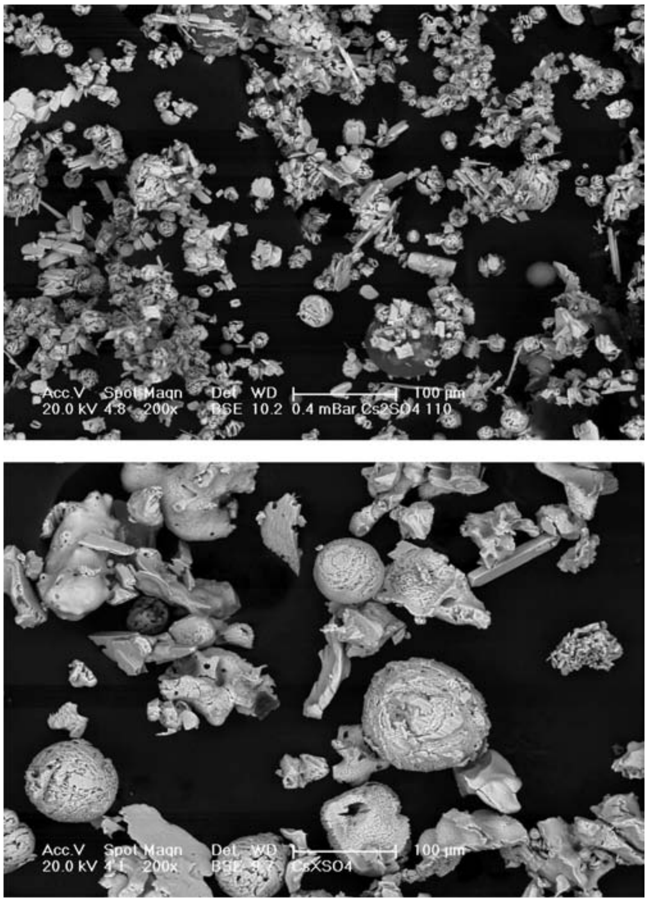

**Figure 4.** Scanning emission microscopy of cesium sulphate (up) and cesium hydrogen sulphate (down) crystals.

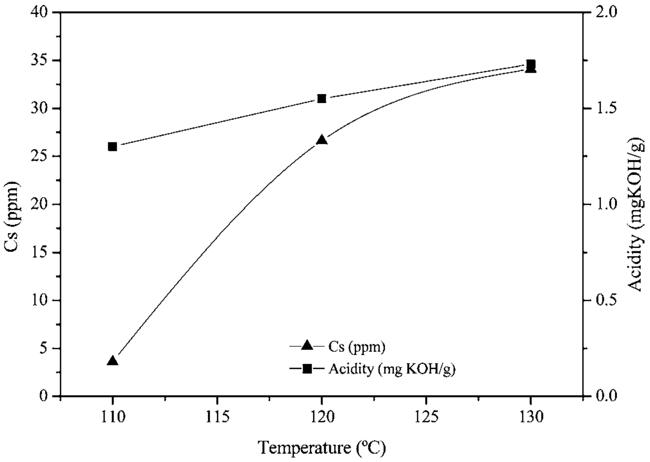

**Figure 5.** Cesium content (ppm) and acidity (mgKOH/g) for different neutralization temperatures (110, 120, and 130 °C).

**3.4. Influence of the Temperature.** In order to study the influence of temperature, the two steps curve of neutralization/dehydration but using three different temperatures (110, 120, and 130 °C) was used. In Figure 5, the final polyol cesium content (ppm) and acidity (mgKOH/g) at different neutralization temperatures are given. As it was confirmed by Rodriguez et al.,[16] only when a neutralization temperature of 110 °C was used, that the cesium content under specification was obtained. When the temperature was increased, crystals were obtained with smaller particle size (18 $\mu$m for 110 °C and 12 $\mu$m for 130 °C). Small particles could cross the filter and be dissolved again by increasing the final polyol cesium content.

Acidity was not within specification whatever the temperature, varying between 1.3 and 1.7 mgKOH/g. The remaining acidity of this polyol F-4811 was out of specification. In our previous work,[16] the polyol F-2831 remained also with a final acidity value from 0.18 to 0.22 mgKOH/g, lower than that for F-4811 but also not into specification.

In any case, it is necessary to develop a system to reduce the polyol acidity by modifying the crystallization procedure or by means a post-treatment of the purified polyol.

## 4. CONCLUSIONS

The parameters of the neutralization process of a 3500 $M_w$ polyol were optimized. In the range of 3−4 wt % of water, the crystals formed had a great size in order to get a suitable filtration. The modification of the dehydration curve parameters did not allow us to obtain a polyol with a cesium content under specification. The neutralization of 3500 $M_w$ polyol was achieved with double the stoichiometric amount of neutralization agent needed, due to the fact that the sulphuric acid reacts only with one proton, forming cesium hydrogen sulphate, as was confirmed by X-ray and SEM. The optimization of the neutralization temperature revealed that a temperature of 110 °C allowed us to obtain a low cesium content.

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### Notes

The authors declare no competing financial interest.

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(17) In our previous work, a polyol 6000 $M_w$ was used. Now, this work is based on the purification of a 3500 $M_w$ polyol that is the polyol grade with the higher production in the company REPSOL. According to the filtration media, a thermostatted stainless steel cartridge, with a 10 cm i.d. and having a 2-L capacity at 130 °C and 245 kN/$m^2$, was fitted with a Sartorius glass-fiber prefilter and a cellulose acetate filter with the capability to retain particles greater than 1 $\mu$m. It is important to notice that at industrial scale the filter should treat up to 100 tons of polyol, so particles <10 $\mu$m pass the filter easily. Therefore, our criterion is based on this size in order to establish a suitable particle size in order to be filtered.

(18) The neutralization of the catalyst in the polyol production using sulphuric acid has been widely studied in our previous works (works cited in the references), confirming that no incorporation of the sulphate groups has been produced. In addition, the integrity of the polyol after the acid treatment and filtration has been confirmed by GPC and the other quality parameters that are conventionally measured. Acid number would not decrease if the sulphonic acid was attached to the backbone of the polyol but is easily eliminated by treatment with an ion-exchange resin. We will explain this aspect in the next work.

(19) The phase behaviour in the neutralization of the catalyst is a complex process taken into account that is a neutralization in polyol media and not in a normal aqueous media. While two phases exist, the aspect of the system is like a white dispersion of water in polyol. The aqueous phase not really soluble in polyol stabilizes the cesium salt due to its high solubility in water. When the amount of water in the polyol gradually decreases, a unique transparent phase appears (a solution of water and cesium salt in polyol) and the nucleation process starts. In this medium, the solubility of the cesium salt might be very small, and therefore, supersaturation is reached. Unfortunately, the solubility values of cesium salt in polyol have not been reported in the literature because is very difficult to acquire a guarantee on the accuracy of solubility experimental data in the polyol phase, and therefore, the supersaturation level could not be quantified.