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Optimization of the Neutralization Process for Cesium Catalyst Removal after Polyol Production

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ABSTRACT: The aim of this study was the optimization of the neutralization process to remove the catalyst cesium hydroxide from crude polyether polyols. Sulfuric acid was chosen as the neutralization agent. First of all, the water content in the neutralization agent solution was optimized. An optimum particle size was obtained for water content between 2 and 3 wt %, and even the cesium content fell within the specifications. Higher water contents cause the solubilization of the cesium sulfate crystals. An increase in the temperature decreased the cesium sulfate particle size, not being retained by the filter and increasing the final polyol cesium content. Acidity was not within specifications whatever the temperature, varying between 0.18 and 0.22 mg of KOH/g. To obtain both parameters (cesium content and acidity) within specification, temperature and time of the dehydration step were modified. An excess of H_2SO_4 allowed us to obtain a suitable particle size for filtration; however, the acidity value was out of specification, suggesting the necessity to find a new process to remove the catalyst in the polyether polyol production.

1. INTRODUCTION

In the preparation of polyols as intermediates for polyurethanes, higher functionality polyols are usually required. The most common initiator is glycerine (three active hydrogen atoms), to produce triols with propylene oxide as monomer and a catalyst.[1] The typical catalyst used in the polyol production, in which the discontinuous batch process is a common practice,[2] is potassium hydroxide. Commonly, a small amount of ethylene oxide is used at the end of the reaction to convert the secondary hydroxyl terminal groups to primary hydroxyls, which have a higher reactivity in subsequent reactions of urethane formation.[3]

This polymerization is anionic, as the growing chain ends in hydroxyl groups, which retain the propensity of growth for at least as long a period as needed for the completion of the synthesis. Hence, the polymerization could be considered as "living polymerization", according to the definition of Szwarc.[4,5] Nevertheless, when the traditional catalysts (K, Na, etc.) are used in the preparation of polyols, the allylic terminal unsaturation appears as an undesirable secondary reaction.[6] 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.

To reduce the unsaturation levels and increase the average functionality, cesium hydroxide can be used as catalyst. Cesium hydroxide has been covered by patents due to its industrial interest.[7−11] Cesium, with a high ionic radius, allows a large separation of the propagating ion pair and favors charge separation. As a result of that, there is an increase in reaction rates and a lower level of unsaturation in the final polyether polyol.[7−15] The improvement of the reaction rate that produces the use of cesium with the subsequent reduction of unsaturation levels allows us to increase the temperature of the process, obtaining an increase in productivity of the industrial facilities.

The main drawback of cesium hydroxide is its high cost compared to the standard; this basic catalyst is approximately 25 times more expensive than potassium hydroxide. Although the amount of catalyst is small, about 1% of the final polyol weight, the high cost of the catalyst, if it is note recycled, makes the process economically unfeasible. Therefore, it is necessary to find a method to recover and reuse the alkali metal compound to provide an economical process.[16]

Regarding the elimination and recovery of the alkaline metal catalysts from polyols, several scientific works can be found in the literature.[15,17−19]

In a previous work,[16] our group demonstrates the technical feasibility of the crystallization process for the removal of the cesium hydroxide catalyst from crude polyether polyols and its recycling. Several acids were tested (hydrochloric, phosphoric, carbonic, and sulfuric acid), sulfuric acid being chosen because its recycling process was easier than with the other acids assayed. In that work, the influence of the water/polyol ratio and the $P-T$ profiles for the polyol neutralization were studied to decrease the process time and to obtain a suitable crystal size. The recycling procedure chosen is based on the precipitation of the sulfate ion with barium hydroxide, obtaining a solution of CsOH that can be recycled to the process.

In this work, the optimization of the CsOH catalyst removal by neutralization with sulfuric acid was made. In this case, the influence of the water content in the neutralization acid solution, the neutralization temperature, and the acid content in the neutralization solution, on the final polyol cesium content and acidity, was studied.

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Table 1. Quality Specifications for Flexible Glycerol Propylene Oxide−Ethylene Oxide Based Polyols

quality parameters	values	test method
cesium content (ppm, max)	10	ASTM D 4668-87
water content (ppm, max)	800	ASTM D 4672-87
acidity (mg KOH/g polyol, max)	0.1	ASTM D 4662-87

2. EXPERIMENTAL SECTION

2.1. Materials. The experiments were limited to the use of a 6000 MW with an EO tip grade polyol, synthesized as described elsewhere[20] with cesium hydroxide as the catalyst. The alkaline metal content in crude form was about 4900 ppm (in commercial terms). Its molecular weight distribution was determined by gel permeation chromatography (GPC). A weight-average molecular weight, M_w, of 6000 was obtained.

Sulfuric acid 95−98% (PANREAC prs-codex grade, Barcelona) was used as the neutralization agent. Methanol was used for washing of the cesium sulfate cake.

2.2. Crystallization Experiments. Batch crystallizations were carried out in a 2 L double-jacketed glass reactor, with digital control of stirring rate and temperature. An agitation device equipped with two Rousthon turbines having six vertical blades was used. The vacuum level was controlled by using a Divatronic DT vacuum indicator−controller, acting on a solenoid valve. The experimental setup was shown in an early work.[16]

Once the crystallization process had finished, the filtration process was carried out in a thermostat stainless steel cartridge, 10 cm i.d. and having a 2 L capacity at 130 °C and 245 KN/m^2, fitted with a Sartorius glass-fiber prefilter and a cellulose acetate filter with capability to retain particles greater than 1 μm.

Quality parameters related to the purification process of polyols were also measured. Table 1 shows the standard quality specifications required for these kinds of products.

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) to reduce their viscosity.

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 μm measurement range is accessed using a single-lens system.

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

An initial operation scheme was devised on the basis of the literature and our previous knowledge of different industrial polyol processes:

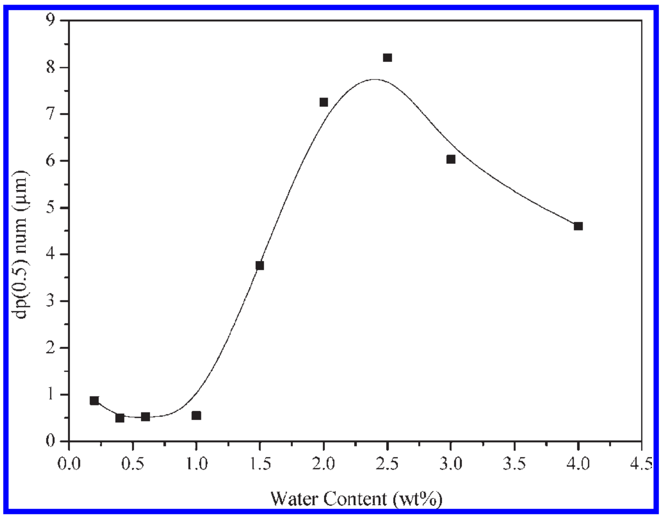

Figure 1. Variation of crystal size with the water content.

- *First Step: Monomers Removal.* Once the polymerization has finished, a small amount of unreacted monomers remains, contaminating the crude polyether-polyol, and they must be removed.
- *Second Step: Neutralization.* If the aim is the formation of crystals, then the second step must be the reaction of the cesium catalyst (polymer bonded) with the neutralization agent solution. An aqueous solution of acid was added to neutralize the polyol, forming initially a water−polyol emulsion. The addition of this solution produced a decrease of the bulk temperature.
- *Third Step: Dehydration−crystallization.* For the elimination of the water in the polyol, a $P-T$ profile protocol of phosphoric acid optimized by A. de Lucas et al.[21] was chosen. It will be called the phosphoric acid curve for simplicity. This curve has been used successfully in processes of neutralization of polyether polyols synthesized with potassium.
- *Fourth Step: Filtration.* Once the crystallization process had finished, the filtration process was carried out. The polyol retained in the filter cake was washed out using methanol for analysis purposes. Then a small sample of the filter cake was collected to measure crystal size distribution. The bottleneck of the industrial process is the time employed in the filtration step, which is logically governed by the crystal size distribution. Thus, the main criterion to select the best operating conditions was the time employed for the filtration of the bulk mixture, expressed as the average mass flow G_m ($kg/(m^2/h)$). The following criteria were proposed, by comparison with the mean times required for the filtration in several industrial polyol processes

$$\text{Fastfiltration}: G_m > 2750\ kg/(m^2/h)$$

$$\text{Mediumfiltration}: 2750 > G_m > 525\ kg/(m^2/h)$$

$$\text{Slowfiltration}: G_m < 525\ kg/(m^2/h)$$

3. RESULTS AND DISCUSSION

3.1. Influence of the Water Content on the Polyol Neutralization with H_2SO_4. The optimization of the water content on the polyol neutralization is the most important factor to

Table 2. Optimization of the Time for the Neutralization and Dehydration−Crystallization, Using 3 wt % of Water, Temperature of 110 °C, and Agitation Rate of 100 rpm

experiment	step	time (min)	dp(0.5) num (μm)	Cs (ppm)	acidity (mg KOH/g)
A	1	30	0.46	6.5	>0.2
	2	60	0.46		
B	1	60	0.45	6.4	>0.2
	2	60	4.67		
C	1	90	4.54	9.6	0.168
	2	60	7.57		
D	1	180	4.69	4.5	>0.2
	2	120	7.96		
C*[a]	1	90	1.43	6.0	0.118
	2	60	5.75		

[a] Agitation rate, 500 rpm.

obtain crystals with a suitable particle size to be filtered. To get the optimum water content, 150 g of polyol was placed in a hermetically sealed vessel, and the temperature and agitation rate were kept under constant value (70 °C and 100 rpm, respectively). As the neutralization agent solution, the stoichiometric amount of H_2SO_4 to form the cesium sulfate was added, and the water content was varied (0.2−4 wt %) to study its influence on the crystallization process.

In Figure 1, the crystal size for the polyol neutralization using different water contents can be observed. After 5 h, when the water content in the neutralization solution was less than 1 wt %, the particle size was less than 1 μm. The solution presented a cloudy aspect, and the cesium content was really low (11 ppm for 0.2 wt % of water) although not lower than that specified by the polyol quality specifications (Table 1). However, for water content in the neutralization solution higher than 1 wt %, a clear solution with well-formed crystals was observed. An optimum particle size was obtained for water content between 2 and 3 wt %, and even the cesium content fell within the specifications from Table 1 (4 and 9 ppm of cesium for 2 and 3 wt % of water content, respectively).

In addition, when water content in the neutralization solution was higher than 4 wt % (at the same latter conditions), formation of cesium sulfate crystals was not observed, due to the solubilization of crystals in water. High water concentration could cause the solubilization of cesium sulfate crystals in water (solubility of 179 g of Cs_2SO_4/100 g of H_2O at 20 °C).

On the basis of these results, batch polyol crystallizations were carried out in a 2 L double-jacketed glass reactor (described in section 2.2). The amount of sulfuric acid used was that stoichiometrically needed to form the cesium sulfate, and the water content in the neutralization solution was 3 wt %, as the optimum water content to form crystal with a suitable size. Experiments were carried out at 110 °C and with an agitation rate of 100 rpm. Two steps were carried out: the first one corresponds to the neutralization step, at atmospheric pressure, and the second one corresponds to the dehydration−crystallization, at pressures below to 10 mbar, removing the water from the polyol and forming the cesium sulfate crystals. The aim was to optimize the time for each step. Therefore, four experiments (A, B, C, and D) were carried out varying the time for the neutralization and dehydration−crystallization. In Table 2, crystal size, cesium content, and acid value for each sample were given. It is clear that when the time of step 1 was increased high particle size was achieved (from 0.46 μm for 30 min to 4.69 μm for 180 min). No difference in particle size between experiments C and D was observed. Therefore, it is possible to conclude that more than 90 min for the neutralization process and 60 min for the dehydration−crystallization process were not needed to increase the particle size. Cesium content fell within the specifications (Table 1) in all experiments (Table 2). Regarding the acidity, only the acidity of the polyol obtained for experiment C was near the limit imposed by the specification (Table 1). For this reason, conditions followed for experiment C were chosen for the rest of the experiences.

The latter experiments (A, B, C, and D) were performed at an agitation rate of 100 rpm observing how a part of the crystal was placed in the bottom of the reactor. To avoid the crystal deposit, a high agitation rate (500 rpm) was tested. At this agitation rate, crystals were well dispersed in the solution, not being closed to the reactor wall. In Table 2, experiments C (100 rpm) and C* (500 rpm) were compared, observing how the crystal size continued being suitable for a correct filtration. Therefore, it is possible to increase the agitation rate without breaking the cesium sulfate crystals.

3.2. Influence of the Temperature on the Polyol Neutralization with H_2SO_4.

The latter polyol neutralizations were performed at 110 °C. In Figure 2, the phase diagrams of the neutralization with H_2SO_4 at three different temperatures (110, 120, and 130 °C) are given. These phase diagrams have been built by observing the state of different water−polyol−salt systems. Four different states were observed: (i) dispersion, where cesium sulfate crystals were deposited at the bottom and the solution was clear; (ii) unstable emulsion, where cesium sulfate crystals were deposited at the bottom and also dispersed on the solution as little particles; (iii) stable emulsion, where the solution was cloudy; and (iv) dispersion−emulsion, as transition state. In all cases, the point represents the state of our polyol dehydration (using 3 wt % of water).

When the neutralization was performed at 110 °C, the water−polyol−salt system was located in the dispersion phase. However, at this temperature, the system was really near the emulsion area. To avoid being in this zone, several experiments at two more temperatures (120 and 130 °C) were realized.

In this case, 600 g of polyol was placed in the 2 L double-jacketed glass reactor, and when the temperature was reached, the polyol neutralization was carried out using the stoichiometric amount of H_2SO_4 to form the cesium sulfate and the optimum water content (3 wt %). The experiments were performed at

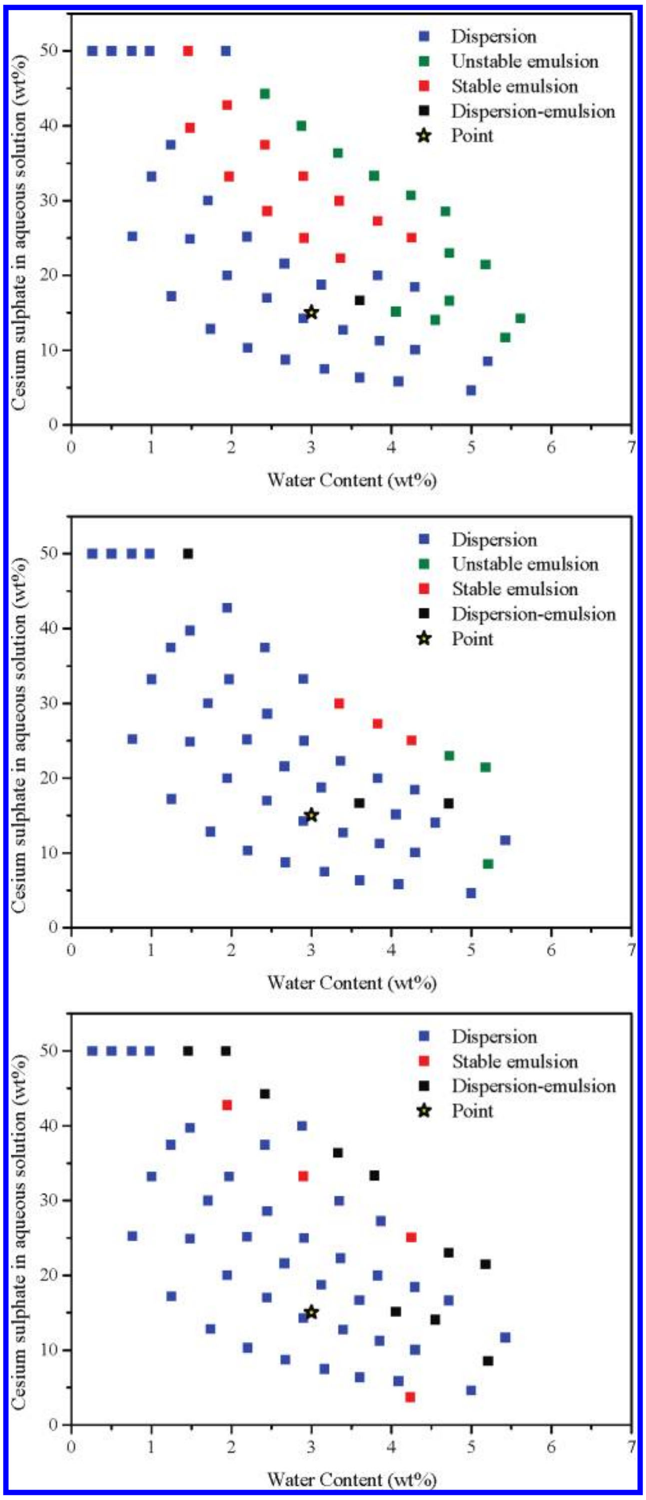

Figure 2. Phase diagrams for the polyol neutralization at 110 °C (above), 120 °C (middle), and 130 °C (bottom).

500 rpm. The neutralization curve was the same as that shown for experiment C (Table 2) but in this case varying the temperature (110, 120, and 130 °C).

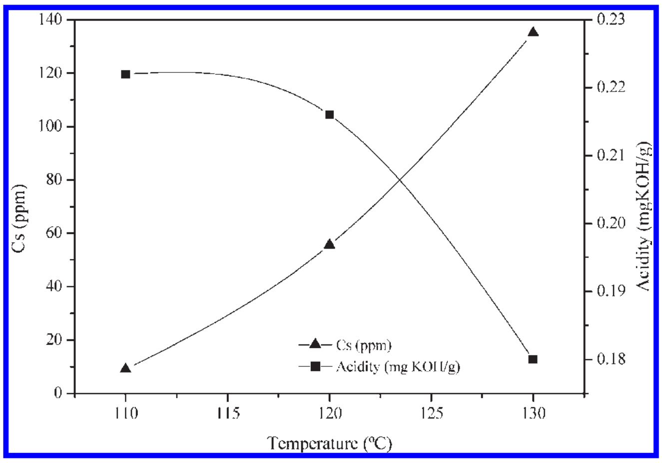

Figure 3. Cesium content (ppm) and acidity (mg KOH/g) for different neutralization temperatures (110, 120, and 130 °C).

In Figure 3, the final polyol cesium content (ppm) and acidity (mg KOH/g) at different neutralization temperatures are given. The main difference was found in the cesium content, this parameter being within specification (<10 ppm) only when the neutralization temperature was 110 °C. The cesium content increased with the neutralization temperature. This fact was due to the decrease of the particle size: when the temperature was increased, cesium sulfate crystals were obtained with smaller particle size, which was corroborated using scanning electron microscopy (Figure 4). The SEM micrographs confirmed the decrease of the particle size with the temperature. Small cesium sulfate particles could cross the filter and be dissolved again increasing the final polyol cesium content.

Acidity was not within specification whatever the temperature, varying between 0.18 and 0.22 mg KOH/g. For this reason, a deep study about the neutralization agent content was performed to obey the acidity specification.

3.3. Influence of the Excess of H_2SO_4 on the Final Polyol Quality. After the optimization of the water content and the neutralization/crystallization temperature, it was possible to obtain a polyol with cesium content within specification. However, the final polyol acidity was always higher than the standard limit (Table 1).

Due to the high acidity value, it was considered to study the exact cesium content in the polyol that, until now, has been calculated from the material balance (theoretical cesium content of 0.4 wt %). If the cesium content is measured by atomic absorption spectrometry (AAS), a value of 0.27 wt % was obtained. To keep the cesium content under specification, the influence of the H_2SO_4 in excess in the polyol neutralization on the parameters like cesium content and acidity was studied.

In Table 3, the cesium content and acidity for different percentages of H_2SO_4 in excess are given. A higher excess in sulfuric acid allowed us to put the final polyol cesium content under specification. However, the acidity was really high (>0.1 mg KOH/g). Nevertheless, when we use the stoichiometric amount of H_2SO_4 (0% in excess), it was not possible to neutralize all the initial cesium content (final polyol cesium content, 177.1 ppm), and the final acidity fell within specification.

To neutralize all the cesium, an excess of 16.3% of H_2SO_4 was chosen, to get low final polyol cesium content (Table 3). To obtain the acidity within specification, temperature and time of the dehydration step were increased to study the influence of the humidity on this parameter. The neutralization step was performed at 110 °C during 90 min, whereas the dehydration step did at 140 °C during 180 min. In Figure 5, the variation of crystal size and humidity with time was given. The particle size obtained

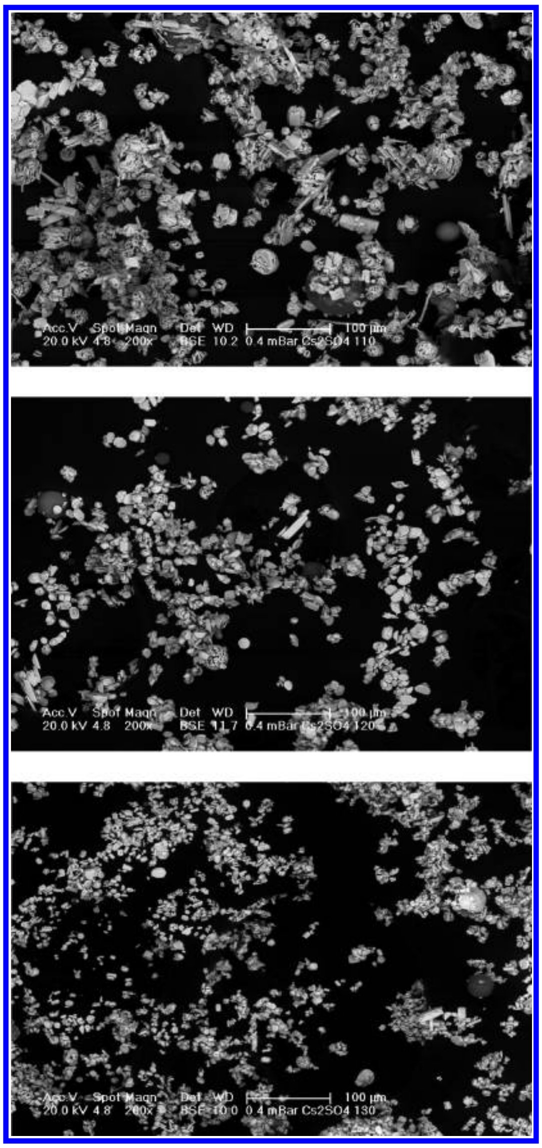

Figure 4. Scanning emission microscopy of cesium sulfate crystals at 110 °C (above), 120 °C (middle), and 130 °C (bottom).

Table 3. Final Cesium Content and Acidity Varying the H_2SO_4 in Excess in the Polyol Neutralization[a]

H_2SO_4 in excess (%)	Cs (ppm)	acidity (mg KOH/g)
0.0	177.1	0.075
8.6	56.1	0.131
16.3	4.2	0.159
21.8	1.8	0.166
36.0	7.0	0.418

[a] Neutralizations were made using 3 wt % of water, temperature of 110 °C, and agitation rate of 500 rpm.

was suitable to get good filtrations. In this case, cesium content lower than 10 ppm was obtained; however, the acidity value (0.180 mg KOH/g) was again out of specification and did not change with the humidity. This parameter met the specification (Table 1, humidity <800 ppm), but a relationship between humidity and acidity was not found.

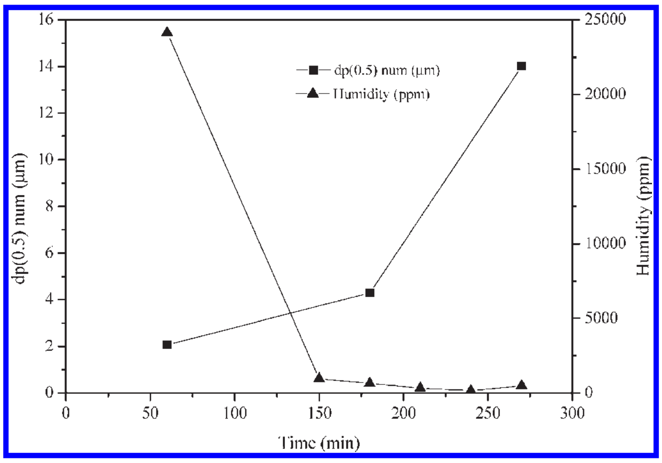

Figure 5. Variation of crystal size and humidity with time.

In our previous study,[16] several neutralization acids were tested, hydrochloric and sulfuric acids being the best options to the catalyst neutralization. Due to the difficulty of the recovery treatment of the cesium salts, sulfuric acid was chosen because of the treatment with barium hydroxide to obtain a cesium hydroxide solution that seems to be the easiest way for cesium recovery. With sulfuric acid, low final cesium content was achieved. However, the final acidity value suggests the necessity to find a new process to remove the catalyst in the polyether polyol production.

4. CONCLUSIONS

The neutralization of polyether polyol was carried out by using sulfuric acid. First, an optimum particle size of cesium sulfate crystals was obtained when water content between 2 and 3 wt % was used. To obtain a suitable particle size, no more than 90 min for the neutralization process and 60 min for the dehydration−crystallization process were needed. An agitation rate of 500 rpm allowed us to avoid the crystal deposition without breaking the cesium sulfate crystals. When the neutralization temperature was increased from 110 to 130 °C, lower particle size was obtained, and the cesium content was out of specification because cesium sulfate particles could cross the filter and be dissolved again, increasing the final polyol cesium content. An acidity value from 0.18 to 0.22 mg KOH/g was obtained, not meeting the specification in any case. Finally, using an excess of sulfuric acid and even higher temperature and time of the dehydration step allowed us to obtain crystals with a suitable size to be filtered. However, the acidity value was again out of specification, suggesting the necessity to find a new process to remove the catalyst in the polyether polyol production.

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