

Preparation and electrochemical study of cerium–silica sol–gel thin films

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Abstract

Design and development of suitable multilayered systems for delaying corrosion advance in metals requires that both the alteration mechanisms of the metal and the behaviour and properties of the protective coatings be known. Coatings prepared by the sol–gel method provide a good approach as protective layers on metallic surfaces. This kind of coatings can be prepared from pure chemical reagents at room temperature and atmospheric pressure, with compositions in a very wide range of environmentally non-aggressive precursors. Sol–gel coatings based on siloxane bonded units were prepared starting from an organic–inorganic hybrid system. The precursors were γ -methacryloxypropyltrimethoxysilane (MAP) and tetramethoxysilane (TMOS). Cerium nitrate hexahydrate in three different concentrations was added. Cerium salts may perform a similar protective effect to that carried out by the well-known lead oxides and chromium salts, even though in this case a negative environmental impact is not expected. Application of coatings upon pure zinc substrates and common glass slides were performed by spinning. Coated samples were heat treated at 40 °C for 6 days. Optical measurements (UV-Vis absorption and diffuse reflectance spectroscopies) pointed out that the coatings were colourless and transparent, reducing the diffuse reflectance of the metallic surface up to ~60%. Optical and scanning electron microscopies (SEM) allowed observation of the texture and microstructure of the coated samples, both before and after the corrosion tests were carried out. Likewise, the remaining sols were kept to gelify at 60 °C for 4 days and then powdered to obtain suitable samples for analysing them by other characterisation techniques (Fourier transformed infrared, FTIR and differential thermal analysis, DTA). Electrochemical measurements were performed by impedance spectroscopy. This technique was used to clarify the anticorrosive protection role of cerium ions incorporated into the hybrid sol–gel network. The effect of cerium concentration on the impedance spectra was analysed, as well as the system behaviour against the corrosive medium (0.6 M NaCl aqueous solutions), as a function of exposure time. From the electrochemical point of view, the sol–gel films behave as a conversion coating on the metallic surface.

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1. Introduction

One of the most common problems at the industrial level is materials damage due to corrosion. Certainly, corrosion can not be avoided but it can be delayed by using new alloys, corrosion inhibitors, protective coatings or by performing cathodic protection. Traditionally, the corrosion delaying strategy employing coatings is based on the application of thick coats that behave as a corrosion barrier. Nowadays,

new trends for design and preparation of protective coatings arise. On the one hand, two general trends are observed: (i) environmental-friendly protection with both non-aggressive materials and production processes [5] and (ii) use of simple low-cost equipments and procedures easily adaptable to the industrial environment [2]. On the other hand, two particular main trends are observed: (i) use of active protective coatings which form new compounds by reaction with the substrate [3] and (ii) self-repairing coatings which form inert compounds by themselves and capable of delaying corrosion advance [4]. For metallic materials an important issue in delaying corrosion advance is the role of *corrosion inhibitors* [5]. These are chemicals that once added in low percentages

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to the protective medium are able to delay corrosion without changes in the physical properties of such medium. In addition, corrosion inhibitors should be non-toxic, inexpensive and easy to handle. Lanthanide salts could be used as corrosion inhibitor pigments. Some research has been done in this field and it is expected that cerium salts will be good candidates as inhibitor pigments for protective coats upon metals [1,6], since they are environmental-friendly compounds with low costs and good compatibility in both organic and inorganic media. It is also expected that this kind of rare earth inhibitor pigments will substitute other toxic conventional protective systems in a few years.

A conventional total anticorrosive paint multilayered system is formed by: (a) an environmentally-resistant painting (top coat), (b) a thick inert barrier (middle layer), (c) an anticorrosive pigment-containing barrier (primer coat) and (d) an electrochemically active interfacial oxide (thin conversion coat). In order to delay corrosion, this latter element in the total anticorrosive multilayered system is extremely important when the failure of the former layers occur due to paint defects, materials ageing, formation of scratches, etc. Conventional passivating conversion coats and primer coats have been introduced by using lead oxides paints and chromium salts. Environmental and safety problems derived from use of such compounds strongly suggest their substitution by environmental-friendly systems, for instance coats containing lanthanide salts.

With the aim to explore new prospective avenues in the topics described above, the objective of the present work was synthesis of thin conversion coatings by the sol–gel method. As it is known, this method can be a good, inexpensive processing route, compatible with other methods commonly used for modification and improvement of metallurgical materials (anodising, galvanising technique, etc.). Moreover, sol–gel coatings can be applied at room temperature and pressure by different, very simple arrangements [7,8]. Cerium nitrate was selected as the most suitable anticorrosive rare earth pigment due to its low cost, compatibility with other raw materials used in the sol–gel process and friendly interactions with the environment. The presented research deals with the physical and chemical characterisation of the coatings prepared by studying their thermal, structural, optical and, especially, electrochemical behaviour [6].

2. Experimental

2.1. Preparation of samples

Zinc panels (15 mm × 15 mm) 1 mm thick were used as metallic substrates. Selection of this kind of substrate is based on the interest of studying both the corrosion phenomena and their delaying, since the galvanised steels top coat is metallic zinc. Energy dispersive X-ray (EDX) microanalysis of the panels surface detected zinc and oxygen that were attributed to the metallic zinc core of the substrates and to

the very thin zinc oxide layer at the surface. Some zinc substrates were polished (600-grit silicon carbide polishing paper), washed with ethanol and coated to obtain samples for optical measurements. Other zinc panels were connected to a wire, resin inlaid, polished by the free surface, washed and coated to obtain samples for electrochemical measurements.

Sols for the coatings were prepared starting from a mixture of 4 mol of tetramethoxysilane (TMOS) and 1 mol of γ -methacryloxypropyltrimethoxysilane (MAP). Methanol and water were added with the molar ratio (TMOS+MAP)/water/methanol of 1/7/8. Finally, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to yield 0.156, 0.625 and 2.500 wt.% Ce^{3+} . The coated samples were labelled coating 1, 2 and 3, depending on their respective Ce^{3+} -content. The coatings application was carried out by spinning using a home-made coater (293 s^{-1} during 10 s) on both inlaid and non-inlaid zinc substrates and upon common glass slides. These latter were made with the aim to perform some optical measurements of the coatings on a transparent substrate. All the coated samples were heat treated at 40°C for 6 days. The remaining sols were gelled at 60°C for 4 days and then grounded to powder. These samples (labelled xerogel 1, 2 and 3) were used to undertake some general physical and chemical characterisation.

2.2. Measurements

The thickness of the coatings before the corrosion treatment was evaluated by the interference fringe method from the corresponding reflexion spectra in the Vis range. UV-Vis absorption and diffuse reflectance spectra (DRS) of the untreated samples were recorded with a Shimadzu 3100 spectrophotometer. Thermal behaviour of the xerogel samples was studied by differential thermal analysis (DTA) and thermogravimetric analysis (TGA), using a Seiko SSC/5200 equipment under air atmosphere. The analyses by DTA were performed on powdered gel samples as the most suitable approach. As it is known, adherence of sol–gel coatings with the zinc substrates is very high. Therefore, detaching the nanosized coating without metallic particles from the substrate was a difficult task. In any case, the study by DTA of the ensemble formed by both the substrate and the coating lies beyond the scope of the present research. Fourier transformed infrared (FTIR) spectra of the xerogel samples diluted in anhydrous KBr (pellets technique) were recorded with a Mattson Galaxy 3020 spectrophotometer.

The coated samples were exposed to a simulated corrosive environment by placing them in an electrochemical cell which contained a 0.6 M NaCl solution. The texture and microstructure of the coatings, both before and after the corrosion tests, were observed by optical microscopy (OM) and scanning electron microscopy (SEM), with an Olympus DP-11 microscope and a Jeol JXA-840 equipment, respectively. Moreover, some EDX microanalyses (Rontec unit, silicon–lithium detector, 15–20 kV) were performed on several areas of the coated samples after the corrosion

treatment. The crystalline phases formed at the samples surface during the tests were detected by X-ray diffractometry (XRD) with a Siemens D-5000 apparatus (40 kV, 30 mA). Finally, the durability of the coated samples was studied by electrochemical impedance spectroscopy (EIS). The experiments were performed using a Solartron 1255 HF frequency response analyser coupled to an EG&G PARC 273 A potentiostat, applying 10 mV amplitude signals over a 10^5 to 10^{-1} Hz frequency range. A three-electrode cell (in which the sample was immersed in a 0.6 M NaCl aqueous solution to study the corrosion phenomena in a simulated marine environment) formed the electrochemical set-up. The reference electrode was a saturated calomel electrode (SCE), the counter-electrode was a platinum disk and the working electrode was the sol-gel coating/zinc system. Measurements were performed as a function of the exposure time (from few hours to 7 days). The interpretation of the obtained impedance spectra has been carried out by computational analysis using the Boukamp program [9].

3. Results and discussion

Optical microscopy of the coatings deposited on glass slides confirmed high level of homogeneity. Small defects on the metallic surfaces were visible through the coatings. Coatings thickness was found to be dependent on the Ce^{3+} -content, in spite of having been obtained at the same spinning rate and time and from the same sol. Average values measured for the coatings 1, 2 and 3 applied on glass slides were 845, 960 and 1185 nm (± 10 nm). UV-Vis spectra of the coatings upon glass slides showed no absorption band in the 250–800 nm range, which indicated that coatings are colourless and transparent. Metallic surfaces usually show high light reflectance, which is often reduced by means of paints and coats. Diffuse reflectance spectra of coatings upon non-inlaid zinc panels (Fig. 1) demonstrated that light attenuation of up to 60% occurred. This result is interesting because, from the point of view of optical properties, the coatings obtained could be properly combined

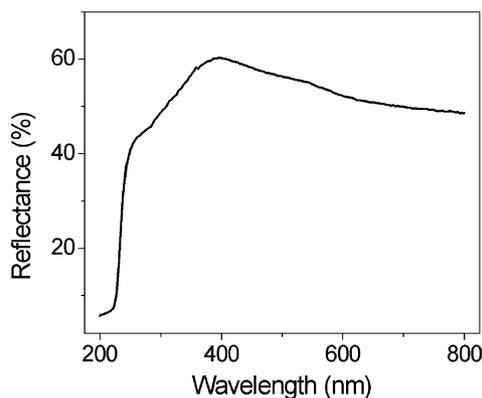


Fig. 1. UV-Vis diffuse reflectance spectrum of a zinc substrate with the coating 2.

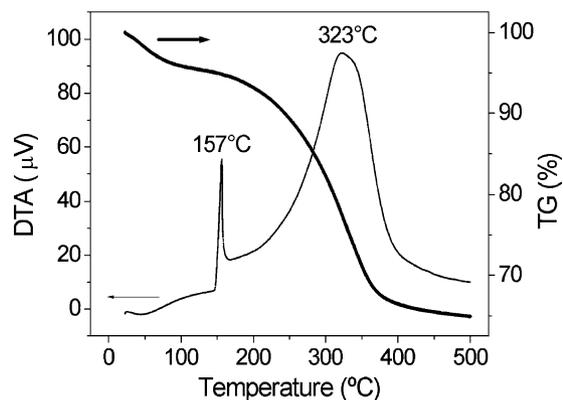


Fig. 2. DTA/TGA curves of the powdered xerogel 1 after heating at 60 °C for 4 days.

with other kinds of final paints or coats without negative interaction, when the attenuation of diffuse reflectance is the main objective.

Fig. 2 shows the DTA/TGA results for the xerogel 1. The first exothermic effect in the DTA curve is attributed to oxidation of the starting silane [10,11] and the second one to the decomposition of the organic groups. The TGA curves showed strong weight losses between 200 and 350 °C which can be attributed to release of the organic matter. In addition, the Ce^{3+} -content dependence has been observed: the higher the Ce^{3+} -content, the lower is the temperature at which the thermal effects occur. This fact could indicate that cerium concentration improved the xerogel densification. In the sol-gel silica network, cerium ions are probably located replacing H^+ ions in silanol groups ($\equiv Si-OH$). Once the coating has been densified, cerium ions could be co-ordinated by six or more oxygen atoms to satisfy the electroneutrality of the glassy network [12]. Thus, this point could explain why the identification degree reached by the samples increases as far as the cerium concentration is higher, since a more closed and interconnected structure is formed.

The FTIR spectra of the xerogels 1, 2 and 3 are shown in Fig. 3. The main features observed as the Ce^{3+} content increased were as follows: ν_{C-O} diminished and $\nu_{C=O}$ and

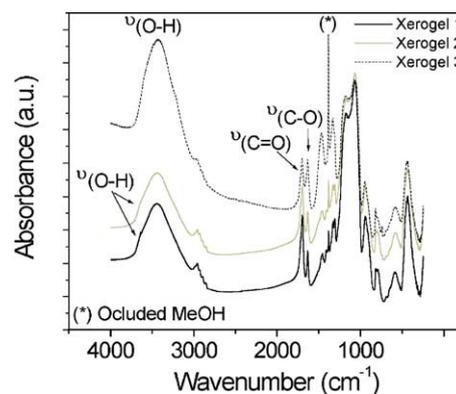


Fig. 3. FTIR spectra of the powdered xerogels 1, 2 and 3 after heating at 60 °C for 4 days.

$\nu_{\text{O-H}}$ increased. Methanol seems to be occluded probably in the gel closed pores, especially for the xerogel 3. The analysis of the bands assignments [13] and their dependence on the Ce^{3+} content indicated that cerium enhanced decomposition of the silane chains via the methacryloxy groups. This yielded the corresponding carboxylic acid depleting the carbonyl groups (the cerium ions could associate with the carboxylate ions).

After the complete corrosion tests with the NaCl solutions, the coated samples were examined by OM and SEM. The exposed zone, which was a circle, appeared with some pits and deposits, especially in the border area near the unexposed surfaces. The pits observed in the treated zone were bigger ($\sim 70 \mu\text{m}$) than those in the untreated area ($\sim 10 \mu\text{m}$). This indicated that deterioration started in the metallic substrate pits, which behave as corrosion nuclei. Moreover, the SEM observations of the deposits revealed a powder-like polycrystalline texture that could correspond to some corrosion product precipitation. The EDX microanalysis of the different areas in the coated samples zone exposed to the NaCl solution showed a silicon content increase in the pits with relatively low amounts of chloride and cerium. On the other hand, the EDX results demonstrated that the higher sodium chloride amounts were at the border deposits, formed during the corrosive treatment.

The XRD results (Fig. 4) performed on the border deposits showed three main crystalline phases: (A), metallic zinc; (B), zinc oxide (zincite); and (C), zinc hydroxychloride (simonkolleite). The corresponding sample was submitted to the complete corrosion test during 7 days. Thus, a very intense corrosive treatment was carried out. Due to the detection limits of the XRD equipment used, the crystallisation of the phases detected could overlap the formation of some cerium precipitates during the first hour of the treatment.

The anticorrosive properties given by the Ce^{3+} -pigments to the sol-gel coatings have been studied by applying EIS. Fig. 5 shows the Bode plots of the experimental impedance spectra corresponding to the coating 1 on the zinc substrate after 1 h exposure to the NaCl solution. The equivalent circuit representing the system presented in Fig. 5 has

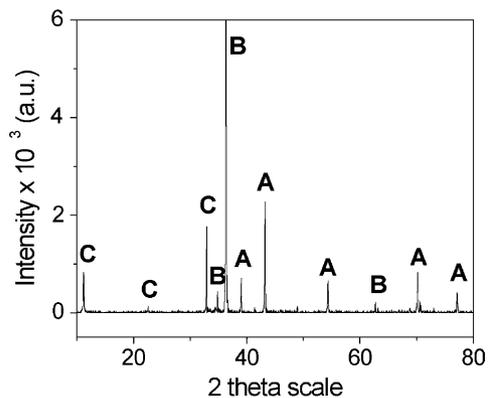


Fig. 4. X-ray diffractogram of the deposits formed after the corrosion test at the border area on a zinc substrate with the coating 2.

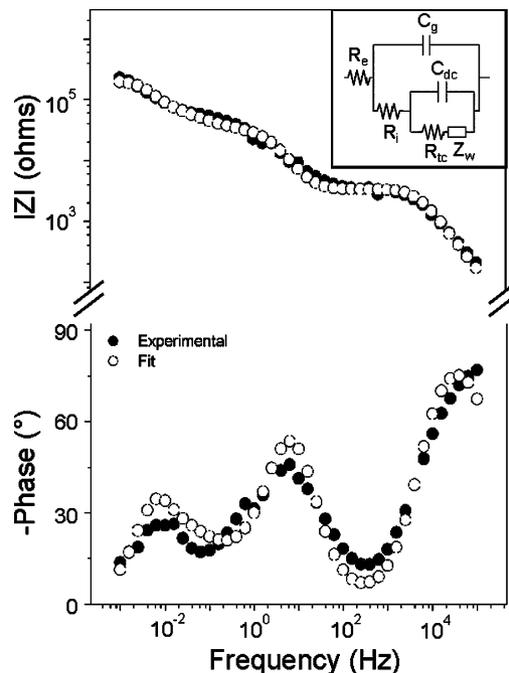


Fig. 5. The Bode representation of the experimental data from the impedance spectra and the fitting results obtained by applying an equivalent circuit for the coating 1 on zinc substrates after 1 h exposure to a 0.6 M NaCl solution.

proved to be suitable to analyse the impedance spectra of the metal/coating systems [14]. In this equivalent circuit, R_e represents the electrolyte resistance, R_i is associated with the ionic resistance of the coating pores, C_g is ascribed to the geometric capacitance of the non-porous coating areas, R_{tc} is the ion-electron charge transfer resistance associated with the corrosion reaction at the bottom of the coating pores, C_{dl} is the electrochemical double layer capacitance at the bottom of the coating pores and Z_w is related to the Warburg diffusion impedance for a finite thickness layer. Fig. 5 also shows the fitting spectrum obtained by applying the former equivalent circuit. The fitted data obtained for the equivalent circuit were as follows: $R_e=5.84 \times 10^1 \Omega$, $C_g=1.00 \times 10^{-8} \text{ F}$, $R_i=3.33 \times 10^3 \Omega$, $C_{dc}=2.65 \times 10^{-6} \text{ F}$, $R_{tc}=2.54 \times 10^4 \Omega$ and, for the Z_w element, $Y_0(O) = 6.02 \times 10^{-5} \text{ (S)}$ and $b(O)=1.06 \times 10^1 \text{ s}^{1/2}$. According to this equivalent circuit it is possible to ascribe physical meaning for each of the three arcs plotted in the Nyquist diagrams (Figs. 6 and 7). The high frequency arcs (HFAs) were associated with the intrinsic electrical properties of the coating (the dielectric constant and the specific ionic conductivity). The middle frequency arcs (MFAs) were associated with the ion-electron resistance of the electrochemical corrosion and to the electrochemical double layer capacitance, both at the bottom of the coating pores. Finally, the low frequency arcs (LFAs) were due to the diffusion phenomena of the electroactive species.

A relationship between the diameters of the arcs and the Ce^{3+} -content in the coatings can be observed (Fig. 6). Thus, after 24 h of exposure to the NaCl solution, the coating 3

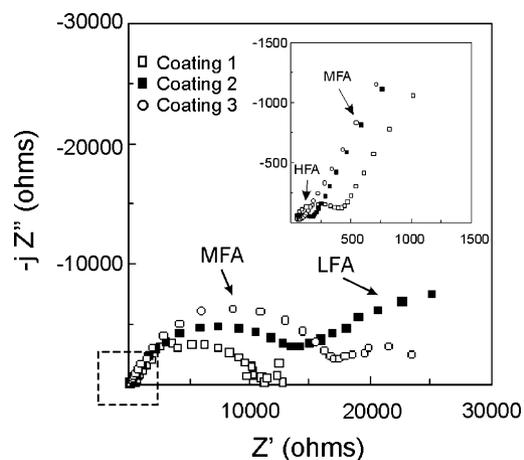


Fig. 6. The Nyquist representation of the impedance data for the different Ce^{3+} containing coatings on zinc substrates, after 1 day exposure to a 0.6M NaCl solution.

showed the lowest HFA diameter (the lowest ionic resistance) (inset in Fig. 6). At the same time, this coating 3 exhibited the highest MFA diameter (Fig. 6). Thus, the coating 3 presents the highest charge transfer resistance (the highest corrosion resistance). Inset in Fig. 7 shows that during the three first hours of exposure to the electrolyte, the HFA diameter of the coating 1 decreased with time. This means that the coating ionic resistance decreased due to the progressive water absorption. On the other hand, Fig. 7 shows that the MFA diameter increased with time. This behaviour indicates that during the first stages (3 h) of exposure to the NaCl solution, the corrosion resistance of the coating 1 increased due to the inhibitor effect of the Ce^{3+} -pigment.

Fig. 8 presents the R_i and R_{tc} values obtained from the impedance measurements as a function of the coatings Ce^{3+} -content and the exposure time to the NaCl solution. The R_i values were obtained from the HFA and the R_{tc} values from the MFA (in both cases by applying the Boukamp system) [9]. Fig. 8 shows that the coating 1 presents both

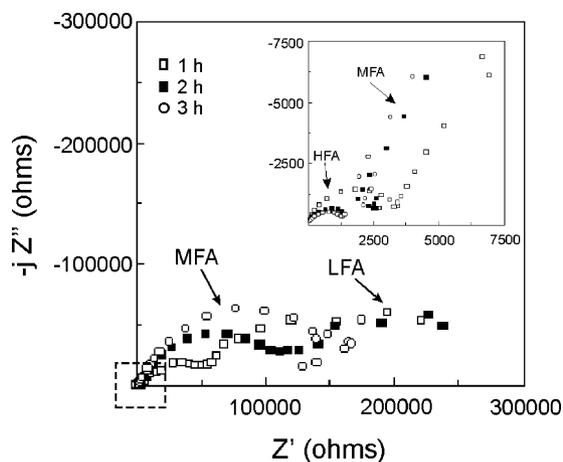


Fig. 7. The Nyquist representation of the impedance data for the coating 1 on zinc substrates for different exposure times to a 0.6M NaCl solution.

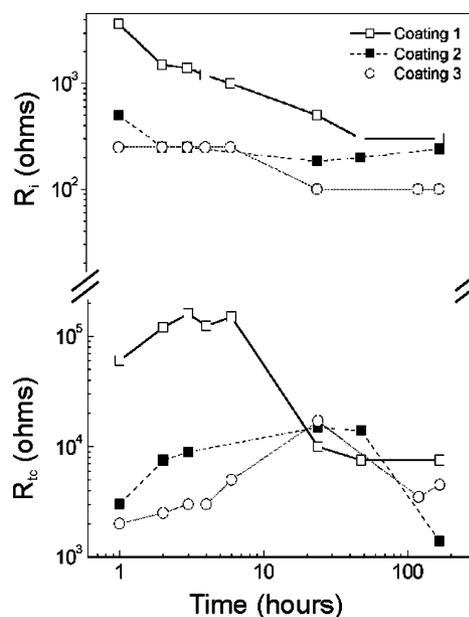


Fig. 8. Evolution of both ionic resistance and charge transfer values with the exposure time to a 0.6M NaCl solution, for the different Ce^{3+} containing coatings on zinc substrates.

the highest ionic resistance and charge transfer resistance during the first 10 h of exposure to the electrolyte. The charge transfer resistance (inversely proportional to the corrosion rate) of this coating increased during the first 8 h of the exposure. This behaviour could indicate that the Ce^{3+} ions showed the corrosion-inhibitor effect when leached from the sol-gel matrix and were deposited at the bottom of the pores. The coatings 2 and 3 show the similar behaviour, even though they displayed lower ionic resistance for short times and after 20–40 h an increased charge transfer resistance. These results demonstrate an evident inhibitor effect of the anticorrosive Ce^{3+} -pigment studied, which could precipitate as insoluble cerium hydroxide at the bottom of the pores. This yielded an increase in the charge transfer resistance that diminished the corrosion rate of the metal/coating system.

4. Conclusions

Hybrid silica sol-gel coatings containing Ce^{3+} -ions behave as a conversion coat on metallic zinc substrates. The critical concentration of the anticorrosive pigment (Ce^{3+} salt) is in the 0.2–0.6 range (wt.%). The higher anticorrosive pigment concentrations could yield networking defects by formation of pigment-coating interfaces, which could retain water. The maximum yield threshold for the anticorrosive pigment has yet to be determined. The anticorrosive performance of the Ce^{3+} ions entrapped in the hybrid silica sol-gel network occurs by means of the inhibitor effect and the self-repairing mechanism (probably with the $\text{Ce}(\text{OH})_3$ precipitation).

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