A Novel Porous Ni, Ce-Doped PbO₂ Electrode for Efficient Treatment of Chloride Ion in Wastewater

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Abstract: The porous Ti/Sb-SnO₂/Ni-Ce-PbO₂ electrode was prepared by using a porous Ti plate as a substrate, an Sb-doped SnO₂ as an intermediate, and a PbO₂ doped with Ni and Ce as an active layer. The surface morphology and crystal structure of the electrode were characterized by scanning electron microscope(SEM), energy dispersive spectrometer(EDS), and X-Ray diffraction(XRD). The electrochemical performance of the electrodes was tested by linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and electrode life test. The results show that the novel porous Ni-Ce-PbO₂ electrodes with larger active surface area have better electrochemical activity and longer electrode life than porous undoped PbO₂ electrodes and flat Ni-Ce-PbO₂ electrodes. In this work, the removal of Cl⁻ in simulated wastewater on three electrodes was also studied. The results show that the removal effect of the porous Ni-Ce-PbO₂ electrode is obviously better than the other two electrodes, and the removal rate is 87.4%, while the removal rates of the other two electrodes were 72.90% and 80.20%, respectively. In addition, the mechanism of electrochemical dechlorinating was also studied. With the progress of electrolysis, we find that the increase of OH⁻ inhibits the degradation of Cl⁻, however, the porous Ni-Ce-PbO₂ electrode can effectively improve the removal of Cl⁻.

Keywords: porous Ni-Ce-PbO₂; co-doping; active surface area; removal rate

1. Introduction

The widespread use of chlorinated compounds such as HCl, NaCl, and MgCl₂ in the industrial field has increased the content of chloride ion in wastewater [1,2]. If it is discharged into the water body beyond control, the water environment will be seriously damaged. The accumulation of chloride ions will make the soil salinized and alkalized, and excessive intake of chlorine by the human body will cause organ damage. Chloride ions are corrosive to pipelines, boilers, etc., and can erode buildings and reduce durability of the concrete structure. For example, a large amount of Cl⁻ in desulfurization wastewater discharged from thermal power plants can corrode pipelines and equipments [3].

At present, the most widely used method for treating Cl⁻ in wastewater is chemical precipitation [4]. However, the concentration of Cl⁻ in the treated wastewater is still high. The treatment of chloride ion in wastewater by chemical precipitation will be limited in the future [5]. How to treat desulfurization wastewater in depth, meet the discharge requirements, and reduce the impact on the environment has always been a difficult problem in the field of wastewater treatment at home and abroad. Therefore, advanced oxidation processes (AOPs) [6,7] such as catalytic ozonation, Fenton oxidation, supercritical water oxidation, electrochemical oxidation, photocatalytic oxidation, etc., [8] have been studied. Electrochemical oxidation is one of the most eye-catching AOPs. It has the advantages of good treatment effect, small floor area, high degradation efficiency, short residence time and no secondary pollution, and has broad application prospects in the advanced treatment of salt compounds and
The degradation efficiency and degradation products of electrochemical oxidation process change with the anode material [11], which means that anode material is one of the main factors in electrochemical oxidation process [12,13]. Because of the critical role of anode materials, scholars have been studying new anodes for many years [14]. The earliest graphite and carbon electrodes have the disadvantages of low current efficiency and poor mechanical strength [15]. Subsequently, metal anodes were developed. At present, metal oxide electrode is widely used and its preparation process is mature, such as dimensionally stable anode (DSA) (e.g., RuO$_2$, IrO$_2$, PbO$_2$, SnO$_2$) [11]. With the deepening of research, 3D porous structure compounds are widely used in the preparation of anode materials because of their large specific surface area, such as carbon nanotubes (CNT), porous graphene (GE), etc., [16,17], which can significantly change the structure of the coating when doped in the metal oxide coating [11]. Scholars have found that doping metal elements in metal oxide coatings can significantly improve the electrode activity and extend service life [18], such as Ce, Bi, Fe, Co, etc., [11]. In addition, it has been found that many rare earth oxides doped into PbO$_2$ can significantly improve the electrochemical performance of the electrode [19]. Kong et al. reported that doping Er$_2$O$_3$, Gd$_2$O$_3$, La$_2$O$_3$, and Ce$_2$O$_3$ on PbO$_2$ electrode could promote the degradation of 4-chlorophenol [20]. Jin et al. [20] found that doping Ce can form smaller crystal size on the surface of the electrode, resulting in the increase of specific surface area and catalytically active sites. Xia et al. [21] reported that proper doping of Ni can make the grains dense, which not only facilitates electron movement, and improves electrochemical performance, but also helps to extend electrode life.

In this work, we intended to use a porous Ti plate as the substrate, because the porous structure has large specific surface area. We can improve the electrochemical activity and stability of the electrode by doping Ce and Ni in the active layer PbO$_2$ electrode [22]. The doping of Ce and Ni reduces the crystal size of the active layer [11,21], but increases the surface area of the active layer and the electrochemical activity of the electrode, in addition, the service life of the electrode is extended to some extent. Finally, the electrochemical activity and stability of porous Ni-Ce-PbO$_2$ electrodes were investigated and compared with the conventional porous undoped PbO$_2$ electrode and the doped flat Ni-Ce-PbO$_2$ electrode. In this experiment, simulated wastewater with high chlorine content was selected as the target pollutant. The electrochemical performance of the electrode was investigated by comparing the effects of three kinds of electrodes on the treatment of chloride ions in simulated wastewater.

2. Experimental

2.1. Materials

Porous titanium plate with a purity of 99.9% was purchased from Baoji Jinkai Technology Co., Ltd., Jinan, China. Ni(NO$_3$)$_2$ 6H$_2$O was purchased from Xiqiao Chemical Co. Ltd., Foshan, China. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All chemicals were of analytical grade and used as received. In this work, deionized water was used in all solutions.

2.2. Electrode Preparation

2.2.1. Titanium Surface Preparation

The porous titanium plates (20 mm × 10 mm × 2.8 mm) bought by Baoji Jinkai Technology Co., Ltd., Jinan, China, had a purity of 99.9% and an average pore diameter of 50 µm to pretreat the substrate. The porous titanium plate was ultrasonically cleaned in acetone for 15 min, washed in 20% NaOH solution at 90 °C for 1 h, and etched in a 15 wt % oxalic acid solution at 90 °C for 1 h until a gray matte titanium matrix was formed, and finally saved in ethanol.

The surface treatment of the flat titanium plate (20 mm × 10 mm × 2.8 mm) is similar to porous titanium plate.
2.2.2. Coating SnO$_2$–Sb$_2$O$_3$

The electrode intermediate layer was prepared by thermal decomposition method [11]. Total of 1.2 g SnCl$_4$, 0.2 g Sb$_2$O$_3$, and 10 mL concentrated hydrochloric acid were dissolved in 25 mL of isopropanol to obtain a precursor-coating solution. The solution was colorless, transparent, slightly sticky. Then the pretreated porous titanium plate was immersed in the precursor solution. After soaking, it was taken out and dried in an oven at 110$^\circ$C, and then calcined in a muffle furnace at 500$^\circ$C for 15 min. After cooling the plate, the drying and calcining process was repeated several times, and the high-temperature baking time in the last time was extended to 1 h to obtain a porous Ti/Sb-SnO$_2$ electrode. The main purpose of this layer is to improve the conductivity of the electrode and prevent the titanium matrix from being oxidized to form TiO$_2$.

The precursor solution can be directly brushed on the surface of the flat titanium plate with a brush. Other preparation processes of the intermediate layer of the flat electrode are similar to that of the porous electrode.

2.2.3. Electrochemical Deposition Ni–Ce–PbO$_2$

Pb(NO$_3$)$_2$, Ni(NO$_3$)$_2$, and Ce(NO$_3$)$_2$ were dissolved in 250 mL water at a ratio of 100:1:1 of Pb, Ni, and Ce. Then, 0.04 M NaF and 4 mL/L of PTFE were added, before adding 0.1 mol/L HNO$_3$ to adjust the pH to 1, to form an electrodeposition solution. The control temperature was 65$^\circ$C, the current density was 20 mA/cm$^2$, the electrodeposition time was 1 h, so as to deposit a surface layer of lead dioxide with Ce, Ni co-doped on the surface of the intermediate layer tin antimony oxide, that is, porous Ti/Sb-SnO$_2$/Ni-Ce-PbO$_2$ electrode.

In addition to the raw materials (Ni (NO$_3$)$_2$ and Ce (NO$_3$)$_2$), the preparation process of porous PbO$_2$ electrode is similar to that of porous Ni-Ce PbO$_2$ electrode.

2.3. Electrode Characterization

The surface morphology was observed using a scanning electron microscope (Quanta 200 of FEI, Hillsboro, OR, USA). X-ray diffraction (XRD) patterns of samples were obtained with an X-ray diffractometer (PANalytical, Almelo, The Netherlands). Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) were performed at room temperature using a computer-controlled electrochemical workstation (CHI 660E, CH Instruments, Shanghai, China) with a conventional three-electrode system. The prepared PbO$_2$-based electrode (20 mm × 20 mm) was used as the working electrode, a saturated Ag/AgCl electrode was employed as the reference electrode, and a stainless steel sheet was applied as the counter electrode. All potentials were referred to the SCE. The stability tests (up to 20 h) were performed by the accelerated life test with a current density of 1 A/cm$^2$ and a temperature of 60 $^\circ$C in 2 M H$_2$SO$_4$ solution for porous undoped PbO$_2$ electrodes, porous Ni-Ce–PbO$_2$ electrodes, and Flat Ni-Ce–PbO$_2$ electrodes. These tests were performed in a three-electrode system.

2.4. Electrochemical Oxidation

A simulated chlorine-containing wastewater with a chloride ion concentration of 4 g/L and a volume of 200 mL was selected as the experimental wastewater; the temperature was 298 K in all experiments. The electrochemical oxidation experiment was conducted by a batch method, and the device was mainly composed of a DC power source, a collector types magnetic stirrer, and a glass reactor. The anode (PbO$_2$-based electrodes) and the cathode (flat titanium plate) were placed parallel to each other and perpendicular to the solution level with a distance of 1 cm. The volume of simulated wastewater in all experiments was 200 mL and the Cl$^-$ concentration was 4 g/L. The temperature of all experiments was maintained at 298 K. All pH values in the experiment were determined by a pH meter and all Cl$^-$ concentration in the experiment were determined by titration with a standard AgNO$_3$ solution.
3. Results and Discussion

3.1. Surface Morphological and Crystallographic Analysis

The SEM images of the plate-modified Ni-Ce-PbO₂ electrode, the porous undoped PbO₂ electrode, and the porous Ni-Ce-PbO₂ electrode are shown in Figure 1. It can be seen that the porous undoped PbO₂ electrode and the porous Ni-Ce-PbO₂ electrode still have many small holes in the electrode surface while compared with porous Ti plate (Figure 1a), indicating that the PbO₂ coating did not block the porous structure. From Figure 1b,f it can be seen that the porous Ni-Ce-PbO₂ electrodes apparently have larger pores and specific surface area compared to the flat Ni-Ce-PbO₂ electrodes.

![SEM images of different electrodes](image)

**Figure 1.** SEM of different electrodes, (a) (porous titanium plate, 80x); (b) (flat Ni-Ce-PbO₂ electrode, 1200x) and (c) (porous undoped PbO₂ electrode, 80x); (d) (porous undoped PbO₂ electrode, 1200x) and (e) (porous Ni-Ce-PbO₂ electrode, 80x); (f) (porous Ni-Ce-PbO₂ electrode, 1200x).
The porous PbO$_2$ electrode doped with Ni and Ce (Figure 1e,f) can make the holes smaller or bigger on the surface of the electrodes, and the specific surface area was larger than porous undoped PbO$_2$ electrodes (Figure 1c,d). Besides, the EDS spectrum of different PbO$_2$ electrodes is shown in Figure 2a, which confirms that there are O, Pb, Ce, Ni elements in the porous Ni-Ce-PbO$_2$ electrode, while there are only O and Pb elements in the porous undoped PbO$_2$ electrodes. Thus, it can be concluded that the Ni and Ce was successfully doped into the PbO$_2$ films and doping of Ni and Ce can reduce the grain size of the PbO$_2$ coating.

![Figure 2. (a) EDS of a (porous PbO$_2$ electrode) and b (porous Ni-Ce-PbO$_2$ electrode); (b) XRD diffraction patterns of different Electrodes A (Porous Ti/Sb-SnO$_2$/PbO$_2$ electrode), B (Porous Ti/Sb-SnO$_2$/Ni-Ce-PbO$_2$ electrode), and C (Standard XRD pattern of PbO$_2$).](image)

From Figure 2b, it can be seen that the diffraction peaks of undoped porous show that dioxide electrodes appear at 25.4 degrees, 31.9 degrees, 36.1 degrees, 48.9 degrees, 58.8 degrees, 62.4 degrees, and 66.8 degrees, which are consistent with the JCPDS card (41–1492) in pattern, indicating that the main component of undoped PbO$_2$ surface layer is $\beta$-PbO$_2$ and the coating of porous Ni-Ce-PbO$_2$ electrode consists of a mixture of crystalline phases of $\alpha$ and $\beta$-PbO$_2$. The content of $\alpha$-PbO$_2$ is higher than that of undoped PbO$_2$ because the doping of Ce changes the preferred crystalline orientation of the electrode surface and forms smaller grains. In addition, compared with the undoped PbO$_2$, the intensity of the diffraction peaks of Ni-Ce-PbO$_2$ decreases or even disappears because of the doping of Ni and Ce. The reason may be that doping of Ni and Ce changes the nucleation and growth of crystals in the coating, making the electrode have smaller crystal size than the undoped PbO$_2$ electrode, which can also be seen from the SEM image. The average crystallite size calculated from the width of [101] diffraction peaks by Scherrer’s formula is 17.64 nm (Ce–Ni) and 28.76 nm (undoped). According to literature [20], the diffraction peak width is inversely proportional to the crystallite size. The result indicates that the deposited Ni-Ce-PbO$_2$ has smaller crystallite size than other electrode. Smaller crystal size may help to form larger specific surface area which may lead to better electrochemical performance.

3.2. Electrochemical Performance Test

As shown in Figure 3a, no redox peak signal was observed on any of the electrodes in the blank Na$_2$SO$_4$ solution, indicating that PbO$_2$ is an electrochemically inert material in the blank Na$_2$SO$_4$ solution. After the addition of Cl$^-$ (Figure 3b), a distinct oxidation peak was obtained. There is no doubt that the oxidation peak is attributed to the oxidation of Cl$^-$ on the surface of the anode. However, no corresponding reduction peak was observed in the reverse scanning from 3 V to 0 V, indicating that the oxidation of Cl$^-$ is a completely irreversible electrode reaction process. The oxidation peak potential of the porous Ni-Ce-PbO$_2$ electrode (2.01 V vs. SCE) was lower than that of the other two electrodes.
(2.24 and 2.48 V), but the oxidation peaks current (0.031 A) was significantly higher than the other two electrodes (0.028 A and 0.024 A), which showed that the porous Ni-Ce-PbO$_2$ electrode has higher electro-catalytic activity for Cl$^-$, and the improvement of its electro-catalytic activity is not only related to the increase in electrode surface area caused by its porous structure and doping with Ni and Ce, but also due to changes in the PbO$_2$ band structure. The electrode doping Ni and Ce not only increases the donor area of PbO$_2$, but also increases the donor level of PbO$_2$, making it easier for electrons to jump from the donor level to the conduction band [21]. Therefore, the conductivity of PbO$_2$ is improved.

Figure 3. (a) Cyclic voltammetry (CV) of different PbO$_2$ electrodes measured in 0.1 mol·L$^{-1}$ Na$_2$SO$_4$ solution, (b) 0.1 mol·L$^{-1}$ Na$_2$SO$_4$ solution (pH = 6.5) containing 4 g L$^{-1}$ Cl$^-$, scan rate: 50 mV s$^{-1}$, $T = 298$ K, (c) LSV curves of different electrodes measured in 0.5 M Na$_2$SO$_4$, scan rate: 10 mV s$^{-1}$, $T = 298$ K, (d) EIS of different electrodes. Conditions: $T = 298$ K, [H$_2$SO$_4$] = 1 M. (e) Electrode stability tests: electrode potential vs. time for the electrolysis using different electrodes. (f) The mass losses of electrodes after accelerated life tests for 20 h.
The oxygen evolution overpotential (OEP) of different electrodes could be measured by LSV. According to the polarization curve in Figure 3c, the OEP of the porous Ni-Ce-PbO$_2$ electrode was the highest with 2.09 V (vs. SCE) compared with the flat Ni-Ce-PbO$_2$ electrode of 1.81 V (vs. SCE) and the porous PbO$_2$ electrode of 1.91 V (vs. SCE), respectively. The electrodes with high OEP values can produce more hydroxyl radicals [23]. In addition, it can be seen from Figure 3c that the porous Ni-Ce-PbO$_2$ electrodes had higher oxygen evolution current than the other two electrodes. The higher oxygen releases current also verified that the active surface area of the porous Ni-Ce-PbO$_2$ electrode is larger than that of the other PbO$_2$-based electrodes.

In Figure 3d, there is an obvious semicircle in the electrochemical impedance spectroscopy (EIS) of the three electrodes. The radius of the semicircle usually reflects the magnitude of the transfer resistance $R_{ct}$ of the chlorine evolution or oxygen evolution reaction, which is available from the EIS spectrum. The $R_{ct}$ sizes of Ni-Ce-PbO$_2$ electrodes, porous PbO$_2$ electrodes, and porous Ni-Ce-PbO$_2$ electrodes were 59.4, 21.2, and 12.2, respectively. It is indicated that the porous Ni-Ce-PbO$_2$ electrode has the best conductivity, the most active surface sites, and the highest chlorine evolution activity.

The service life is a critical factor in the practical application of the electrode. Under the condition of anode current of 1A cm$^{-2}$ and temperature of 60 $^\circ$C, the accelerated life test of different PbO$_2$ electrodes was carried out in 2M H$_2$SO$_4$ solution for 20 h. According to Figure 3e,f, the Ni-Ce-PbO$_2$ electrode exhibited better electrochemical stability and less mass loss than the pure PbO$_2$ electrode. It is well-known that the main reasons of mass loss of electrode are the separation and dissolution of PbO$_2$ film, and the mass loss is proportional to the service life of the electrode. Therefore, it can be concluded that the stability of Ni-Ce-PbO$_2$ electrode is much better than that of pure PbO$_2$ electrode by the modification of Ni and Ce. The mass loss of the porous Ni-Ce-PbO$_2$ electrode is slightly larger than that of the flat Ni-Ce-PbO$_2$, mainly because of the loose porosity of the structure. In fact, in the experiments, we found that film peeled off on the pure PbO$_2$ electrode, but not on the other two modified PbO$_2$ electrodes.

3.3. Electrochemical Oxidation of Cl$^-$ in Simulated Wastewater

The electrochemical oxidation of simulated wastewater was compared with three kinds of electrodes. From Figure 4a, after electrolysis for 100 min, the removal rate of Cl$^-$ on the porous Ni-Ce-PbO$_2$ electrode was as high as 87.4%. At the same time, the plate Ni-Ce-PbO$_2$ electrode and the porous PbO$_2$ electrode were used as anodes, and the highest removal rates of Cl$^-$ were 72.90% and 80.20%, respectively. Obviously, the above results show that the electrochemical oxidation ability of the porous Ni-Ce-PbO$_2$ electrode was much higher than the other two electrodes. This may be due to the fact that the porous structure increases the surface area of the electrode and the doping of Ni and Ce further increases the surface area of the electrode, which facilitates the adsorption of Cl$^-$ on the surface of the anode and promotes the mass transfer and exchange of the reactants. Thus, the electrochemical oxidation ability of the electrode is improved. As is shown in Figure 4b that in the early stage of electrolysis, the removal rate of Cl$^-$ was higher than that in the later stage because of the enrichment of Cl$^-$ in wastewater. The results show that higher current density result in higher Cl$^-$ removal rate, and the difference in Cl$^-$ removal rate was not obvious at relatively higher current densities. With the progress of electrolysis, the decrease of Cl$^-$ concentration inhibited the oxidation of Cl$^-$ and reached equilibrium at a certain time, in which Cl$^-$ cannot be completely removed. However, the porous Ni-Ce-PbO$_2$ electrode with large specific surface area can effectively improve the removal rate of Cl$^-$. During the process of degradation of Cl$^-$, the chlorine evolution reaction and oxygen evolution side reaction in the anode proceed simultaneously, the content of Cl$^-$ is higher and the content of OH$^-$ is lower in the initial stage of reaction process (Figure 4c). The reaction formulas are as follows:

Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ (1)

$\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}_3\text{O}^+ + \text{Cl}^-$ (2)
The increase of OH− concentration promotes the disproportionation of chlorine and forms a large number of ClO− (Equations (2) and (3)). In addition, Figure 4a also shows the fact that the Cl− removal rate increases significantly with the increase of the initial concentration. But after the electrolysis time reaches 90 min, a large amount of Cl− is removed and the OH− concentration in the solution is gradually increased. This can also be seen from Figure 4c,d, the reaction formulas are as follows:

\[
\begin{align*}
\text{Cathode:} & \quad 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \\
\text{Anode:} & \quad 2\text{OH}^- \rightarrow 4\text{H}^+ + \text{O}_2 \\
\end{align*}
\]

A large amount of OH groups accumulates on the surface of the anode, which hinders the contact between a small amount of Cl− in the solution and the anode, so that the oxygen evolution reaction on the surface of the anode gradually becomes the main reaction. The consumption of OH− on the anode results in a small part of residual Cl− in the solution which cannot be removed, and another
small part of Cl\(^{-}\) is converted into ClO\(^{-}\) and HClO [24] (Equations (1)–(3)), which greatly limits the removal of Cl\(^{-}\). Also as a DSA electrode, the porous Ni-Ce-PbO\(_2\) electrode degraded 87.4% of Cl\(^{-}\) at 90 min because of its large active surface area, while the degradation rate of the plated Ni-Ce-PbO\(_2\) electrode and the porous PbO\(_2\) electrode were only 72.90% and 80.20%, respectively. Therefore, the porous Ni-Ce-PbO\(_2\) electrode breaks through the limitation of the conventional electrode in removing Cl\(^{-}\). In addition, we also detected the concentration of Pb\(^{2+}\) and Ni\(^{2+}\) in the solution after the 5th oxidation, and found that the concentration of Pb\(^{2+}\) was only about 0.0085 mg/L, and Ni\(^{2+}\) was even less, far lower than the standard of the World Health Organization. It shows that it is environment friendly and will not cause secondary pollution.

4. Conclusions

In this paper, porous Ni-Ce-doped PbO\(_2\) electrodes were successfully prepared on a porous titanium substrate by thermal deposition and electrodeposition. The surface morphology, crystal structure, electrochemical activity, and electrode stability of the flat Ni-Ce-PbO\(_2\), porous undoped PbO\(_2\), and porous Ni-Ce-PbO\(_2\) were tested, and the electro-catalytic properties of these three electrodes in simulated wastewater were compared.

The porous Ni-Ce-PbO\(_2\) electrodes possessed porous structure and smaller grain size than the other two electrodes. The doping of Ni and Ce can change the nucleation and growth of crystals on the surface of the electrode, making the electrode have smaller particles, larger electrochemical active surface area, and better electrode life.

At a current density of 50 mA, the porous Ni-Ce-PbO\(_2\) electrode was used to treat Cl\(^{-}\) in the simulated wastewater. The removal rate was as high as 87.4%, while the highest removal rates of the porous pure PbO\(_2\) electrode and the flat Ni-Ce-PbO\(_2\) electrode were 72.90% and 80.20%, respectively.

In addition, in the later stage of Cl\(^{-}\) oxidation, because of the increase of pH of the electrolyte, oxygen evolution reaction mainly occurs in the anode, which results in a part of Cl\(^{-}\) that cannot be removed from the solution and the other part that dissolves in the solution in the form of ClO\(^{-}\) and HClO; removal rate of Cl\(^{-}\) is restricted. The novel porous Ni-Ce-PbO\(_2\) electrodes can effectively improve the removal of Cl\(^{-}\) because of its greater electrochemically active surface area.

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