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Mercury Removal from Concentrated Sulfuric Acid by Electrochemical Alloy Formation on Platinum

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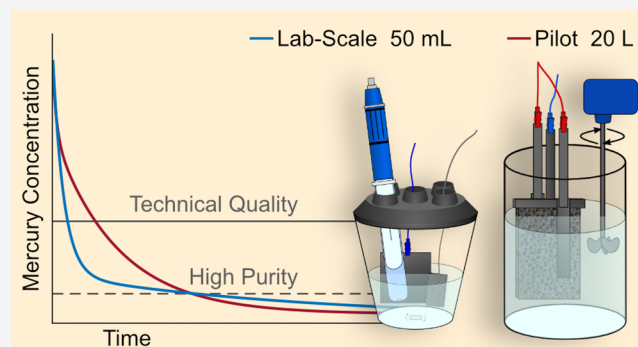
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Supporting Information

ABSTRACT: Mercury is a highly toxic heavy metal, and improved removal processes are required in a range of industrial applications to limit the environmental impacts. At present, no viable removal methods exist commercially for mercury removal of aqueous solutions at high acidic conditions, such as concentrated sulfuric acid. Herein, we show that electrochemical mercury removal based on electrochemical alloy formation on platinum, forming PtHg₄, can be used to remove mercury from concentrated sulfuric acid. Thin platinum film electrodes and porous electrodes with supported platinum are used to remove more than 90% of mercury from concentrated acid from a zinc smelter with an initial mercury concentration of 0.3–0.9 mg/kg, achieving high-quality acid (<0.08 mg/kg) within 80 h. The removal process is carried out in 50 mL laboratory-scale experiments and scaled up to a 20 L pilot reactor with retained removal efficiency, highlighting excellent scalability of the method. In addition, the removal efficiency and stability of different electrode substrate materials are studied to ensure high-quality acid and a long lifetime of the electrodes in harsh chemical conditions, offering a potential method for future large-scale mercury decontamination of sulfuric acid.

KEYWORDS: mercury removal, sulfuric acid, electrochemistry, alloy formation, platinum



INTRODUCTION

Sulfuric acid (93–98%) is one of the most widely used chemicals in the world with an annual production of more than 200 million tonnes per year, with applications in, e.g., mining, fertilizer, and paper industries. Sulfuric acid is mainly produced from sulfur dioxide gas via a so-called contact process, where sulfur dioxide is made by burning of fossil fuels or it can exist as a by-product from zinc and copper smelting processes.^{1–3} When sulfuric acid is produced by the metal producing industry, it can be highly contaminated as the ore can contain varying amounts of metals such as chromium, nickel, copper, zinc, lead, manganese, cadmium, arsenic, and mercury.⁴ Using the method of roasting in smelting, the mercury from the ore is volatilized as mercury vapor and it exits with the off gases and enters the product acid.^{5,6} This mercury contamination can to some extent be mitigated using gas phase cleaning methods. However, these methods can be expensive and are often not sufficient to completely remove mercury from sulfuric acid below the required limits.^{7,8} For commercial applications, sulfuric acid is considered to be of technical-quality grade with regard to mercury when its content is below 0.30 mg/kg and high-purity grade when the content is below 0.08 mg/kg.⁴ Depending on the application of sulfuric acid, the remaining mercury can end up in the produced product and/or in the

waste streams from the processes and can, thus, be spread to the environment and increase the risk of human exposure.⁵

Mercury is a heavy metal with high toxicity and bioaccumulation and is widely dispersed in the environment, posing a serious threat to all living organisms.^{9–11} Mercury can be emitted to the environment through natural sources, such as volcanic eruptions and rock weathering. However, emissions through anthropogenic sources, such as mining and smelting plants, are substantially higher than natural ones and it is estimated that 1,130,000 tonnes of mercury was released into the environment through anthropogenic sources between the years 1850–2010.¹² In 2015, the global annual emissions from anthropogenic sources were estimated to be 2220 tonnes, with 300 tonnes emitted from nonferrous metal production.¹³ During the last decades, efforts have been made to reduce the emissions of mercury; however, it persists in the environment as mercury released years ago is still circulating in the

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environment today. After its initial release into the environment, surfaces such as land and water can repeatedly re-emit mercury into the atmosphere, where mercury can be transported vast distances. As a result, mercury does not only have an impact on a local scale, but it is a global concern, affecting millions of people's lives and their environment around the world.^{14–16}

Current established methods for mercury decontamination of aqueous solutions are far from ideal. These methods include adsorption, precipitation, coagulation, electrodialysis, flocculation, flotation, ion exchange, and membrane filtration, each with their own advantages and disadvantages. Depending on the application, the main drawbacks can include low selectivity for mercury, poor efficiency at very low mercury concentrations, and cost efficiency.^{17–20} Some methods are also highly pH-dependent, e.g., for effective sulfide precipitation, a pH of 7–9 is needed, and for methods involving adsorption, the optimum pH ranges between 4–5.²¹ In addition, the materials used for most adsorption methods, as well as ion-exchange and membrane separation methods, can degrade when used to treat concentrated acids. Thus far, no commercial solution has been presented for removing mercury from concentrated acids, such as sulfuric acid.²⁰

We have recently introduced an electrochemical mercury removal technique based on electrochemical alloy formation which was shown to be able to remove mercury from aqueous streams with pH between 0–6.6.²² In this study, we continue further development of this removal method by examining for the first time its potential to remove mercury from concentrated sulfuric acid, both from synthetic samples and authentic industrial acid produced from a zinc smelter.

■ EXPERIMENTAL SECTION

Fabrication of Working Electrodes. For laboratory-scale experiments, electrodes made of polished fused silica glass (Mark Optics Inc.) (15 × 30 × 0.5 mm), stainless-steel plate 316L (SS316L) (15 × 25 × 1 mm) (Harald Pihl), SS316L 45 PPI foam (15 × 25 × 5 mm) (Alantum, Fraunhofer IFAM), and a Duocel reticulated vitreous carbon (RVC) 60 PPI foam (15 × 40 × 5 mm) (ERG Aerospace) were used. The glass electrodes were coated with 100 nm of platinum with 3 nm titanium adhesion layer using physical vapor deposition (Lesker PVD 225 e-beam evaporator, base pressure $\sim 10^{-7}$ mbar). A pattern of titanium and platinum was created on the glass electrode using deposition masks consisting of a 15 × 15 mm square at the bottom of the substrate with a 1 mm connector strip to the top, where the contact was made. Both the SS316L plate and the RVC foam were coated with 200 nm of platinum with 2 nm of titanium as the adhesion layer using a PVD sputter system (Nordiko 2000 sputter). In addition, for a control experiment, an RVC foam without platinum coating was used. The SS316L foam was coated with approximately 1–2 μm of platinum with 2 nm of gold as the adhesion layer using a high-temperature electrolysis process in a molten salt solution in a commercial process performed by the company Umicore. A thin SS316L wire (0.5 mm) was attached to the top part of the SS316L and RVC foams for electric contact, while for the glass and SS316L plate electrodes, contact was established by using a polymer-covered copper wire attached with copper-conductive tape and sealed with hot glue, as described earlier.²² For pilot experiments, an SS316L foam material (210 × 270 × 3 mm) (Alantum, Fraunhofer IFAM) was coated with platinum by Umicore in the same process as

described above. Photographs and further information about the electrodes used can be seen in the Supporting Information (SI).

Electrolyte Preparation. Concentrated sulfuric acid from a zinc smelting plant in Kokkola, Finland, was provided by Boliden, and used as received for experiments both at the laboratory scale and pilot. At laboratory-scale (50 mL) experiments, three different batches of acid with initial mercury concentrations of approximately 0.3, 0.8, and 0.9 mg/kg were used. For the pilot-scale experiments (20 L), the acid batch had an initial mercury concentration of 0.8 mg/kg. Synthetic concentrated sulfuric acid (97%, Suprapur, Merck) with an initial mercury concentration of 0.8 mg/kg was used at the laboratory scale for experiments using the RVC foam electrode without platinum. In addition, synthetic acid with an initial mercury concentration of 5.5 mg/kg was used for electrode analysis.

Analytical Techniques. The concentration of all metals in solution was analyzed using inductively coupled plasma mass spectrometry (ICP-MS; iCAP-Qc, Thermo Fischer). X-ray diffraction (Siemens Diffraktometer D5000) was used to investigate the platinum glass electrode before and after electrochemical treatment.

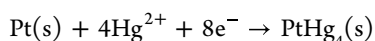
Electrochemical Experiments. Laboratory Scale: 50 mL Cell. All experiments at the laboratory scale were performed using a three-electrode system with 50 mL of concentrated sulfuric acid as the electrolyte. Fused silica glass plate, SS316L plate and foam, as well as RVC foam-supported Pt electrodes were used as the working electrode (WE), with a Pt wire or a diamond electrode (DIACHEM, Condias) as the counter electrode (CE), and a Ag/AgCl (SI Analytics, B3610+) electrode as the reference electrode (RE). A potentiostat (Gamry Reference 600) was used to apply a constant potential of +0.18 V vs the reversible hydrogen electrode (RHE). This potential of +0.18 V vs RHE was chosen to provide a large overpotential for electrochemical alloy formation,^{22–24} while avoiding hydrogen evolution reaction (HER). With HER, gas bubbles could cover parts of the electrode surface and hinder further mercury reduction, as less surface area is available on the electrode. The experiments were performed at a temperature of 20 °C and with active stirring using a glass-covered magnetic stirrer. Samples were taken from the electrolyte before, during, and after the experiments for ICP-MS analysis of Hg, Fe, and Pt contents. Each time, a sample of 100 μL was removed from the electrolyte and diluted with 1 M hydrochloric acid (prepared from Suprapur 36%, Supelco HCl, and Milli-Q water, $>18\text{ M}\Omega/\text{cm}$) with 2 $\mu\text{g}/\text{L}$ bismuth (Bi Internal Standard in 2% HNO_3 , 10 mg/L, VHGLabs) to a concentration with a dilution factor of 50 in the interval of 0–33 $\mu\text{g Hg}/\text{L}$, for ICP-MS analysis. A schematic illustration and photographs of the laboratory cell can be seen in the SI.

Pilot Scale: 20 L Cell. All pilot-scale experiments were performed with a two-electrode setup in a 30 L SS316L reactor (Denios) containing 20 L of concentrated sulfuric acid as the electrolyte. Two SS316L foams were used as the cathode with two diamond-coated Si electrodes (200 mm × 20 mm × 6 mm) (DIACHEM Condias) as the anode. A bench top power supply (EA Elektro-Automatik) was used to control the potential or current applied to the electrodes. Two separate pilot experiments were performed: one with a three-electrode setup using the potential control and one with a two-electrode setup using the current control. For simplification, the cathode and the anode are referred to as the working electrode (WE)

and the counter electrode (CE), respectively, both in the two-electrode setup and the three-electrode setup. A Ag/AgCl reference electrode (RE) was used during the setup of the potential control experiment to achieve the same potential of the WE as in the laboratory-scale experiments. The voltage between WE and CE was adjusted during the first couple of hours of the experiment but was kept constant at -2.98 V from 2.5 h forward. During the current control experiment, a constant current of -0.7 A was applied to the WE to achieve roughly the same current density as in the laboratory-scale experiments. Experiments were performed at temperatures varying in the range 13 – 16 °C and with a propeller stirrer (IKA EUROSTAR 40 digital, 3-bladed 316L) at 500 rpm. Samples were taken from the electrolyte before, during, and after the experiment for ICP-MS analysis of the Hg, Fe, and Pt contents. Each time, three samples of 100 μ L were removed from the electrolyte and diluted to a concentration suitable for ICP-MS analysis, as described above. A schematic illustration and photographs of the experimental setup can be seen in the SI.

RESULTS AND DISCUSSION

Mercury Removal and Alloy Formation in Concentrated Sulfuric Acid in a 50 mL Laboratory Cell. It has previously been shown that mercury containing aqueous solutions can be efficiently decontaminated using a method based on an electrochemically induced formation of an alloy between mercury in solution and a platinum cathode electrode, in the thermodynamically favored phase PtHg_4 .²⁵ The mechanism between platinum and mercury during electrochemical alloy formation has been discussed in the literature previously.^{22–27} It can be described as a multi-step process, where divalent mercury ions are reduced to elemental mercury on an electrode's surface when sufficient potential is applied to form an alloy with platinum. The overall chemical reaction for the formation of PtHg_4 is



This technique has the potential to offer several important advantages over established methods, e.g., it has been shown that the alloying process is not affected by pH (in the interval 0 – 6.6). The method has high efficiency, extremely high selectivity for mercury, and is able to remove mercury in solutions with initial mercury concentrations down to 50 $\mu\text{g/L}$. The process is reversible, and thus, the electrodes and platinum can be regenerated and reused.²² However, the technique has not been applied to concentrated acids before, where it could be expected that high acidity might make the mercury ions more stable in the acid than in the alloy.

To evaluate the possibility of using electrochemical alloy formation to remove mercury from highly acidic streams, concentrated sulfuric acid with an initial mercury concentration of approximately 0.30 mg/kg was decontaminated using a 15×30 mm active area of a platinum-coated fused silica glass (Pt/Glass plate) electrode with an applied potential of $+0.18$ V vs RHE, and the results are shown in Figure 1a. It can be observed that more than 80% of the mercury content was successfully removed from the acid within 140 h as the mercury concentration was reduced from the initial 0.30 mg/kg to a final concentration of 0.06 mg/kg. This means that the process was able to decrease the mercury concentration well below technical quality and even below high purity.

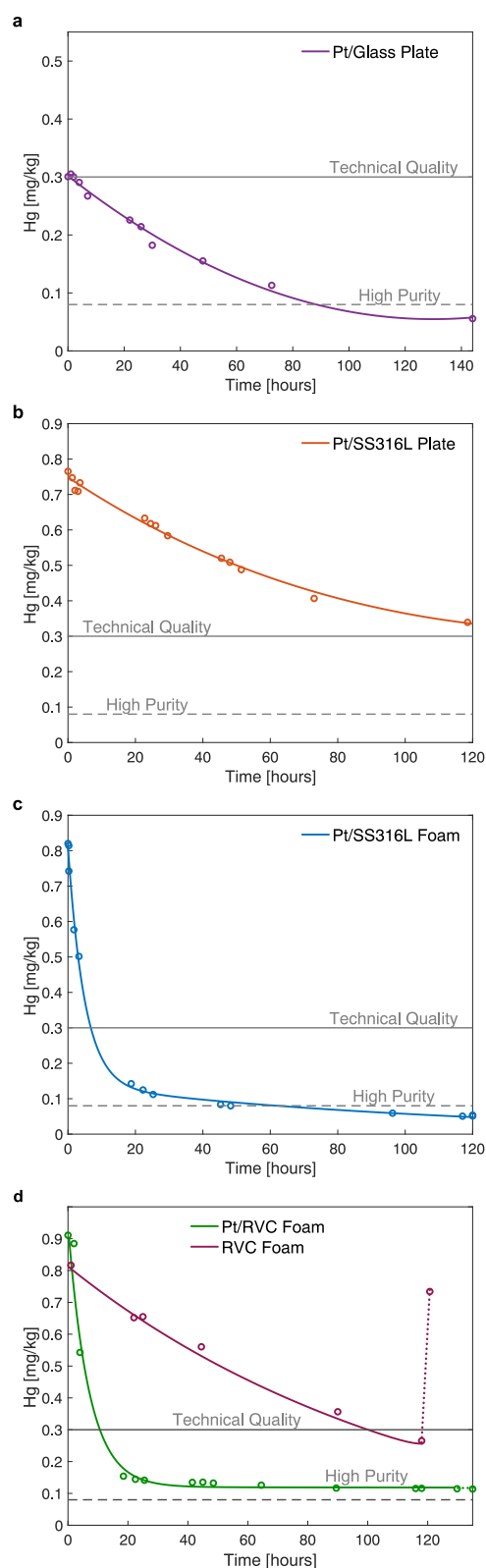


Figure 1. Mercury removal at the laboratory scale (50 mL) using (a) a Pt/glass electrode (15×30 mm) and (b) an SS316L plate (15×25 mm), as well as two different foam materials: (c) SS316L foam (15×25 mm), where technical quality (0.30 mg/kg) of the acid is reached within 20 h and targeted high-purity quality (0.08 mg/kg) within 80 h. (d) RVC foam (15×40 mm) and RVC foam without platinum coating. Solid lines represent the time where the potential (0.18 V vs RHE) was applied to the working electrode (0 – 118 and 0 – 123 h for RVC and Pt/RVC foam, respectively) and dashed lines correspond to

Figure 1. continued

the time when the potential was removed from the electrode (118–123 and 133–134 h for RVC and Pt/RVC foam, respectively). For Pt/RVC foam, technical quality (0.30 mg/kg) of the acid is reached within 20 h, and high-purity quality (0.08 mg/kg) is not quite achieved. The curve fittings serve as a visual aid without representing the best fit of the data spread.

In order to confirm that the alloy formed in concentrated sulfuric acid is in the phase PtHg_4 , as previously shown in diluted acids,²² an additional removal experiment was performed at the laboratory scale with a Pt/Glass plate electrode. The electrode was characterized with X-ray diffraction (XRD) before and after electrochemical mercury removal in concentrated acid, and the XRD pattern obtained can be seen in the SI. To obtain clear and visible XRD patterns, the 100 nm platinum film was saturated to approximately 25% of its theoretical PtHg_4 saturation limit using sulfuric acid with an initial mercury concentration of 5.5 mg/kg. The results show the presence of PtHg_4 after electrochemical mercury removal from concentrated acid.

For practical applications, a thin platinum film on glass is not a viable electrode design as all current needs to be conducted laterally in the thin platinum film and, thus, the electrode is very sensitive to scratches and wear. For industrial applications, it would be desirable to use a conductive substrate with strong adhesion to platinum and with a relatively low price. Potential support materials for platinum include high-quality corrosion-resistant stainless steel, such as SS316L and Reticulated Vitreous Carbon (RVC), both shown to have excellent corrosion resistance in concentrated sulfuric acid at room temperature.^{28–30}

To assess the possibility of using SS316L as a support material, a 15 × 25 mm platinum-coated SS316L plate (Pt/SS316L plate) electrode was used to decontaminate concentrated sulfuric acid with an initial mercury concentration of approximately 0.80 mg/kg, and the results are shown in Figure 1b. The Pt/SS316L plate was observed to be stable in the concentrated acid, and the process was able to remove around 60% of mercury in 120 h, reducing the initial concentration from 0.76 mg/kg to a final concentration of 0.32 mg/kg. Thus, it can be concluded that platinum-coated SS316L can be used as the working electrode in the mercury removal process. However, in this experiment, with an initial mercury concentration of 0.80 mg/kg and an electrode active area of 15 × 25 mm, it was not possible to reach technical or high purity quality within 120 h. Had the experiment been conducted for a longer time, or if a larger active surface area electrode had been used, it is most likely that the mercury concentration would have been reduced below both technical- and high-purity quality.^{18,22} For practical applications, short process times are desired and, thus, the most viable path is to use electrodes with a much higher surface area than the flat glass and steel plate electrodes. The platinum needs to be deposited onto a high surface area support to increase the rate of mercury removal and minimize the amount of platinum required, as precious metals such as platinum come at a very high cost. It can be noted that the mercury removal rate from the plate electrodes Pt/SS316L, presented in Figure 1b, is very low, approximately 0.3 $\mu\text{g}/\text{cm}^2$ h for an initial concentration of 0.8 mg Hg/kg. This estimation of the removal rate is based on the difference between the first two data points (Figure 1b),

after one hour of electrochemical treatment and divided by the area of the electrode used.

Foam materials are a type of material that offers a very high surface area, and by using a 15 × 25 mm platinum-coated SS316L foam (Pt/SS316L foam) electrode for the removal experiment, over 90% of the mercury content was removed within 120 h. The mercury concentration was reduced from an initial 0.80 mg/kg to a final concentration of 0.05 mg/kg, and technical quality was achieved within 20 h and high purity within 80 h, as shown in Figure 1c. Comparing the removal rates between the platinum-coated SS316L plate and foam (Figure 1b,c), it is clear that the rate is enhanced around 10 times for the foam, due to its large surface area. Thus, it can be stated that a platinum-coated foam electrode can be used to remove mercury well below the technical- and high-purity target levels from concentrated sulfuric acid at a rate suitable for industrial processes.

However, in these experiments, it was found that the SS316L foam was unstable in the concentrated acid during mercury removal, as iron, to a large extent, and platinum, to a minor extent, was found to leach from the electrode during the experiment, as discussed further below. As an alternative support material, a 15 × 40 mm platinum-coated RVC foam (Pt/RVC foam) electrode was used instead of the SS316L foam to decontaminate concentrated sulfuric acid with an initial mercury concentration of approximately 0.9 mg/kg. Using an RVC foam material, which is a metal-free carbon material, instead of the SS316L foam or other metal electrode materials, will prevent potential metal ion contamination of the acid from the cathode electrode. The results are shown in Figure 1d, where around 90% of the mercury content was removed from the acid within 120 h to yield a final concentration of 0.10 mg/kg. Technical quality of the acid was reached within 20 h. In this experiment, the mercury concentration appears to level out and not decrease below 0.10 mg/kg, a value just above the targeted high-purity quality. Up to 20 h, the mercury removal for the RVC foam is very similar to that for the SS316L foam, and it is somewhat unexpected that the mercury concentration does not continue to decrease as much for the RVC foam after 20 h. A possible explanation could be that when platinum is deposited on a surface of a porous substrate, the platinum film thickness will vary from virtually zero up to the nominal thickness of the deposited material. During the removal process, the part of the foam with the thinnest platinum layers will get saturated, leading to a less platinum surface area on the surface being able to absorb mercury, which could lead to lower removal rates. In addition, the deposition for the RVC foam was performed from only one side of the foam material; thus, the porous foam has limited coverage and the available platinum surface is likely much smaller for the RVC foam than for the SS316L foam. With an improved coating technique, it is likely that the Pt/RVC foam electrodes would enable a mercury concentration well below that of the targeted high-purity quality.

In order to show the mercury removal process without platinum on the working electrode, an additional experiment was performed with a pure RVC foam electrode without platinum coating in 50 mL of synthetic concentrated sulfuric acid with an initial concentration of 0.8 mg/kg, and the result can be seen in Figure 1d together with the platinum-coated RVC. It is clear that with an applied potential, the mercury concentration in the acid is reduced also on the electrode without platinum, but at a much lower rate compared to the

Pt/RVC foam electrode. This is most likely a result of regular mercury ion reduction to metallic mercury in the porous RVC structure and trapping of mercury in the porous structure. However, the mercury that is plated or attracted to the electrode is not stable in the absence of platinum, and when the potential is turned off, the mercury concentration rapidly increases to the original concentration (the dashed line in Figure 1d). This is in contrast to the case with a platinum-coated RVC where the mercury removal is much faster, and mercury is stable on the electrode also after the potential is removed. In this case, the mercury concentration remains at the lowest value also after turning off the potential. It is clear that with platinum on the electrode, it is possible to form a stable alloy also in highly acidic conditions as well as decrease the mercury concentration of the acid.

While these results are very promising, they reflect mercury removal from concentrated sulfuric acid via electrochemical alloy formation at the laboratory scale (50 mL). To be used in real applications, the method needs to be scaled up to treat hundreds or even thousands of tonnes of concentrated sulfuric acid within given time constraints.

Electrode Stability during Mercury Removal. As indicated above, the Pt/SS316L foam was found to release relatively large amounts of iron and a small amount of platinum during the removal experiment. Figure 2a shows iron and mercury concentrations in sulfuric acid during the removal process and as can be seen, iron continuously leached out of the foam and after about 60 h, the concentration of iron in the acid had increased from an initial value of about 16 mg/kg to above the technical quality limit given for iron, 30 mg/kg. At 120 h, the iron concentration had increased to approximately 48 mg/kg, which is unacceptable from a commercial point of view and indicates that these electrodes would have a limited lifetime. It can also be noted that the relatively high initial iron levels (about 16 mg/kg) in this batch of acid were higher than the iron limit for high-purity quality (15 mg/kg). In addition, platinum was found to also leach out of the SS316L foam material, where the concentration rapidly increased at the start of the removal process when the potential was applied but seemed to level off after 1–2 h and stay constant at about 0.03 mg/kg for the rest of the experiment, as can be seen in Figure 2b. It is likely that at least part of the leached platinum from the Pt/SS316L foam results from corrosion of the foam support, but it might also originate from inhomogeneities in the deposition process where some platinum might have low adhesion to the substrate. It is important to note that after the initial expel, the remaining platinum on the electrode appears to be stable, and despite the continuous leaching of iron, no additional platinum is lost during the rest of the removal process. It is difficult to identify the reasons for the low stability of the SS316L foam, and it is also unexpected since other forms of SS316L are used globally to store and handle sulfuric acid in industry. A potential explanation might be that the foam did not have the stated high-quality SS316L structure and composition throughout the material due to defects from fabrication or as a result of the high-temperature plating process.

The Pt/RVC foam material demonstrated excellent stability in the concentrated sulfuric acid. The material is a carbon-type foam, insoluble in concentrated acid, and thus, iron or other metals leaching out is not an issue in this case. Similar to the Pt/SS316L foam, platinum leached out of the Pt/RVC foam at the start of the removal process and after 120 h, the platinum

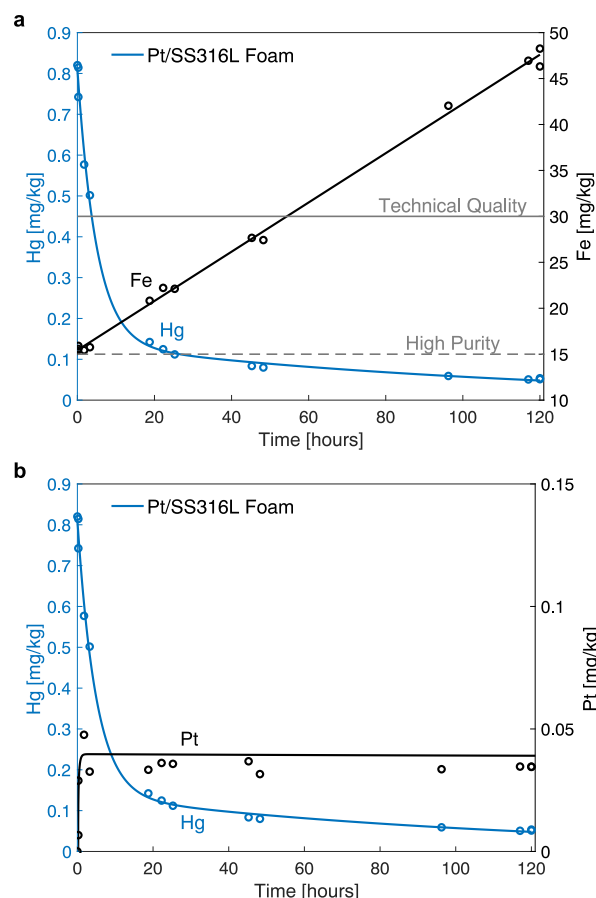


Figure 2. Stability of the Pt/SS316L foam (15 × 25 mm) during mercury removal at the laboratory scale with the corresponding increase in concentration for iron (a) and platinum (b). The iron concentration rapidly increases above high-purity quality (15 mg/kg) and after about 60 h, the concentration reached above the technical limit (30 mg/kg). The platinum concentration jumps (0.05 mg/kg) when a potential is applied to the system and then remains somewhat stable throughout the 120 h. No high-purity technical limits are given for platinum. The curve fittings serve as a visual aid without representing the best fit of the data spread.

content in the acid was about 0.03 mg/kg. Again, this can originate from the deposition process itself where some of the platinum might have low adhesion to the substrate. The results for the Pt/RVC foam can be seen in the SI.

Mercury Removal and Alloy Formation in Concentrated Sulfuric Acid in a 20 L Pilot Reactor. To assess the prospects of implementing the electrochemical mercury removal process at a larger scale, the laboratory-scale experiments in a 50 mL reactor, as described in the previous sections, were scaled up 400 times to a reactor able to treat 20 L of concentrated sulfuric acid, which will be referred to as a pilot reactor. The pilot experiment was performed two times and yielded similar results in both cases; one was performed using potential control and the other using current control. The results from the latter experiment are presented and discussed here in this section, while the results from the former can be seen in the SI.

Concentrated sulfuric acid with an initial mercury concentration of approximately 0.75 mg/kg was decontaminated using Pt/SS316L foam electrodes and a constant current of -0.7 A, over the span of 7 days. Figure 3a shows mercury removal with the change in mercury concentration in the 20 L

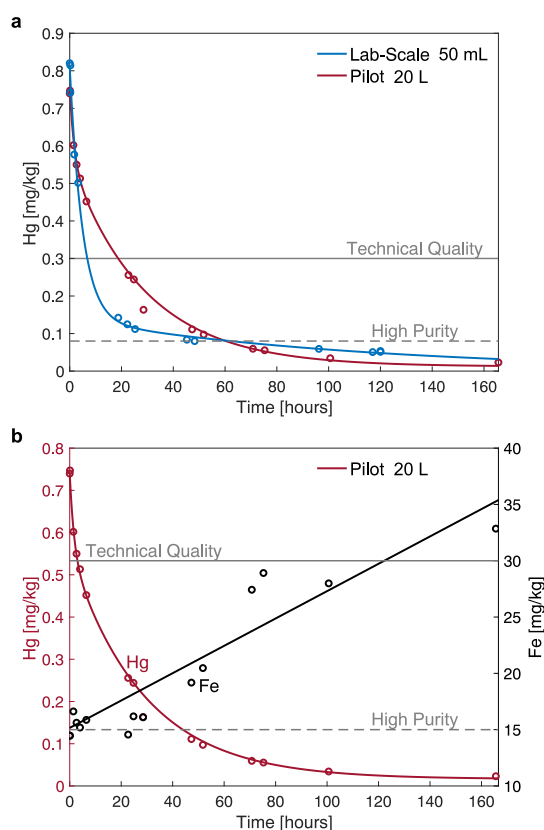


Figure 3. Mercury removal from concentrated sulfuric acid using Pt/SS316L foam electrodes, where (a) the blue curve corresponds to mercury removal at the laboratory scale (50 mL), while the red curve represents removal in a 20 L pilot reactor. In both cases, technical quality (0.30 mg/kg) of the acid is reached within 24 h and high-purity quality (0.08 mg/kg) within 80 h. (b) Red curve corresponds to the mercury removal in a 20 L pilot reactor, while the black curve is the corresponding increase in iron concentration. After 120 h, the iron concentration in the pilot increases above technical quality (30 mg/kg). The curve fittings serve only as visual aids without representing the best fit of the data spread.

pilot as well as the results at the laboratory scale using a similar Pt/SS316L foam electrode (data from Figure 1c). The decrease in mercury concentration and the corresponding increase in iron concentration during the pilot removal process are presented in Figure 3b.

It can be observed that mercury is successfully removed from the 20 L reactor of concentrated sulfuric acid as well. The experiment removes over 98% of the mercury content within 160 h and technical quality is reached around the 20 h mark and high-purity quality within 80 h. The rate of mercury removal in the pilot reactor is initially very similar to the rate measured at the laboratory scale; however, after 10 h, the rate of removal in the pilot becomes lower and technical quality is achieved slightly later than that at the laboratory scale.

After 60 h, the removal trend becomes similar and high-purity quality is achieved in both cases at similar times, within 80 h. There are several possible reasons for the small differences in removal behavior between the laboratory scale and pilot reactor experiments, (i) the cathode electrode area vs electrolyte volume was approximately 40% larger in the pilot experiment which should result in an increased removal rate. (ii) The temperature during the pilot experiments varied between 13–16 °C, while at the laboratory scale, it was

constant at 20 °C, something that should result in a lower reaction rate and slower mercury removal in the pilot experiment.¹⁸ (iii) In the pilot reactor experiments, two rather small anode electrodes were used in contrast to one of roughly equal size to the cathode electrode, as was used in the laboratory-scale experiments. (iv) The geometry of the reactors and the mixing of the acid were different in the two experiments, which could also impact the rate of removal. Despite these differences, it is observed that the removal process largely follows the same trend and reached mercury concentrations well below technical and high-purity quality during the experiments. Similar to the mercury removal at the laboratory scale using the Pt/SS316L foam electrode, the iron concentration in the acid increases almost linearly throughout the 7 days, increasing above the iron technical limit of 30 mg/kg after 120 h. It can be noted that the quality of the concentrated sulfuric acid was again poor to begin with in terms of iron contamination, as the iron concentration in the acid was initially above the iron high-purity limit of 15 mg/kg. To avoid increased iron contamination of the acid, the pilot experiment could have been carried out using the Pt/RVC foam material as experiments at the laboratory scale showed promising results. However, Pt/SS316L foams were more readily available of the size and quality needed for the pilot than the Pt/RVC foams. Despite Pt/SS316L foams lacking stability in the concentrated acid at the laboratory scale, mercury removal was still excellent, and thus, the material was used to evaluate the scalability of the removal method in a 20 L pilot-reactor.

The pilot experiments confirm excellent scalability of the technique, while maintaining the same efficiency. The technique's scalability is crucial for commercialization, and these results show the technique's potential for real applications, where it needs to be further scaled up to treat hundreds or even thousands of tonnes of sulfuric acid.

CONCLUSIONS

Using a novel method based on electrochemical alloy formation on platinum, over 90% of the initial mercury content was removed from commercial concentrated sulfuric acid from a smelting plant, achieving high quality of the acid with respect to mercury content below important industrial limits of 0.30 and 0.08 mg/kg. The method was successfully employed at the laboratory scale, where mercury was removed from 50 mL of concentrated sulfuric acid below a technical quality limit of 0.30 mg/kg and a high-purity quality limit of 0.08 mg/kg, within 80 h. The method was scaled up 400 times from the laboratory scale to a 20 L pilot reactor and concentrated sulfuric acid was again decontaminated below technical and high-purity quality limits within 80 h. This confirmed scalability indicates that the method has great potential for industrial-scale applications, treating thousands of tonnes of concentrated sulfuric acid, which has never been demonstrated before. It can also be mentioned that the electrochemical alloy formation process is reversible, and the electrodes can be regenerated by reversing the electrical potential and releasing the mercury in a controlled way and, thus, allow reuse of the electrodes. However, to consider this novel method for applications at a larger scale, finding a suitable support material for the platinum electrode is of paramount importance to ensure high quality of the treated sulfuric acid and long-lasting electrodes that can survive several cycles of mercury removal and regeneration. A potential

candidate, a stainless-steel foam (SS316L), was shown to offer efficient mercury removal; however, the material was discovered to have poor corrosion resistance to the concentrated acid and thus unsuitable for future applications. An alternative support material, a carbon foam (RVC), displayed efficient mercury removal without corrosion or degradation of the material in the concentrated acid, presenting a very promising candidate as the support material for the platinum electrode for further development at large-scale mercury decontamination.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestengg.2c00417>.

Additional experimental details; electrode materials; methods; uncertainties; and illustrations and photographs of the experimental setup (PDF)

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Author Contributions

V.R., J.J., A.A., and B.W. contributed to the preparation of the electrodes and the design of the experimental process. V.R. and J.J. conducted the electrochemical experiments, and V.R. conducted the ICP-MS analysis. All authors discussed the results and wrote the manuscript.

Notes

The authors declare the following competing financial interest(s): (1) a patent application (EP 17199244.9) has been filed, and B.W. is listed as one of the inventors. (2) The startup company Atium is currently developing a commercial water treatment system based on the patent, with B.W. as one of the minority owners and A.A. working in product development. (3) The industrial samples obtained from Boliden Kokkola where J.N. and J.S. are employed.

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