Recovery of noble metals from industrial process waters by the use of functional textiles

Opwıs K.[1*], Mayer-Gall T.[1], And Gutmann J.S.[1]

[1]Deutsches Textilforschungszentrum Nord-West gGmbH, Adlerstr. 1, D-47798 Krefeld, Germany

*corresponding author:

e-mail: Opwis@dtnw.de

Abstract

The recycling and recovery of high-prized noble metals such as platinum, gold, palladium and silver or rare and strategic metals like indium, gallium, and rare earth metals from scrap metals and wastewaters will be from steadily increasing importance within the next years. Therefore, the focus has to be set on the detection of potentially usable secondary resources and the development of inexpensive and energy-saving processes to separate and recover the metals selectively (urban mining). Beside electronic scrap industrial process and wastewaters represent a considerable source for noble metals. Recently, we have successfully developed an innovative metal-adsorbing textile filter material based on polyvinylamine-coated polyester fibers. The surface modification of the fibrous material is easy to realize with common methods in textile finishing yielding a durable, high-performing and even cheap adsorbent for water-dissolved metal ions. We present results on the general textile finishing procedure and the pH-depending adsorption of noble metal ions. The feasibility of the overall process is demonstrated on palladium containing process waters obtained from a German producer of curcuit boards. Moreover, the same innovative adsorber material is useful for the decontamination of chromate-polluted ground waters and soils. Our latest investigations focus their use in the selective recovery of rare earth metals from large-scale FCC catalyst production for the petroleum refining industry.

Keywords: textile, polyelectrolyte, metal recovery, urban mining, textile mining

1. Introduction

The recycling and recovery of high-prized noble metals such as platinum, gold, palladium and silver or rare and strategic metals like indium, gallium, niobium, tantalum and rare earth metals from scrap metals and wastewaters will be of steadily increasing importance within the next years (and decades). Therefore, one big issue is the detection of potentially usable secondary resources and the development of inexpensive and energy-saving processes to separate and recover the metals selectively. Beside electronic scrap industrial process waters and wastewaters represent a considerable source for noble metals. Various strategies for their recovery such as ion exchange, precipitations, extractions, electrolytic procedures and pyrometallurgical processes plus combinations already exist [1-3]. For the regeneration of rinsing waters and the tail end cleaning of wastewaters ion exchangers are typically used. The high-value metals can be enriched and afterwards recovered by other techniques. However, such solutions often contain comparatively high amounts of nonferrous metals, which strongly limit the economic use of ion exchangers because the insufficient selectivity leads to a rapid charging mainly with the undesired nonferrous metals. During electrolytic metal recovery the dissolved metal ions are precipitated elemental at the cathode by applying direct voltage. The cost effectiveness of the procedure strongly depends on the metal ion concentration. Low concentrations leads to poor space-time yields. Moreover, undesired side reactions at the anode, e.g. the generation of chlorine, may hamper the electrolysis. However and despite the mentioned disadvantages, electrolysis is often applied when high-value noble metals have to be recovered. In such cases the high attainable current yield and the high market value of the metals surmount the investment and maintenance costs. An almost complete metal recovery is only achievable by accepting very poor current yields and, therefore, high costs. Especially in the case of low-concentrated industrial rinsing waters an additional, cost-intensive enrichment by vaporization, ionic exchange or the application of membrane processes is needed. Chemical precipitations for metal ions as hydroxides or sulfides are suitable, when all individual metals can be precipitated separately. In industrial waters this is typically not the case, so that a crude mixture of different products arises. In addition, the precipitations can be highly disperse (e.g. in the case of tin). For a better separation flocking agents are used, which leads to a strong increase of the total waste amount. After an initial separation process typically another fine filtration or treatment by selective ionic exchangers is required. The final pyrometallurgical metal recovery of the hydroxide and sulfide cakes can be carried out in various furnaces. During liquid-liquid-extraction the metal-containing solution is mixed with an organic hydrophobic phase from which the metal ions can be recovered as aqueous concentrates by stripping with acids. The enriched solution can be processed by electrolysis or direct pyrometallurgical metal recovery. However, the extraction process is accompanied with complex chemical pretreatments and large-scale plants. Due to the mentioned disadvantages and the poor selectivity the recycling of low-concentrated industrial process and rinsing waters is often not worthwhile using the existing metal recovery methods. For that reason it was the goal of several BMWi and BMBF financed research projects to develop a new textile-based adsorber material for the selective enrichment and recovery of precious metals from industrial rinsing and wastewaters. This was conducted by the finishing of textile substrates with various polyelectrolytes. Such species are able to bind the target metals such as gold, platinum, palladium or silver selectively in high amounts by ionic interactions or complex formation. Moreover, the recyclability of the adsorber textile was investigated and compared with a direct combustion of the metal-loaded textile followed by a metallurgical processing.

2. Methods used

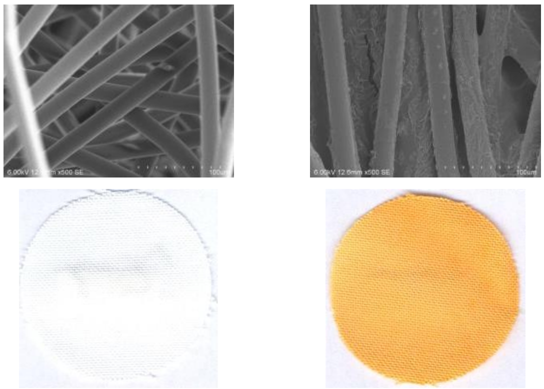
A commercial polyester (PET) non-woven textile with surface weight of 350 g/m^2 was wetted with a high-concentrated commercial polyvinylamine (PVAm) solution under alkaline conditions, pre-dried and afterwards thermally fixed. To remove non-bonded PVAm the material was washed with water and surfactants at 60 °C. At certain pH values (3 - 13) the metal adsorption behavior of the modified textile was tested from various model waters containing K_2PtCl_4, H_2PtCl_6), $KAu(CN)_2$, $HAuCl_4$, $AgNO_3$, $KAg(CN)_2$, $PdCl_2$ and Na_2PdCl_4 (metal concentration each 1 mmol/l). The absolute metal loading has been determined by ICP/OES after microwave digestion. In Addition, analogous investigations were carried out using real palladium containing process waters obtained from a producer of curcuit boards (Pd concentration ca. 400 mg/l).

3. Results

3.1. Finishing of PET fibers with polyvinylamine and adsorption of noble metals

Different natural and synthetic polyelectrolytes were immobilized permanently on various textile materials using thermal and wet chemical techniques. Especially the fixation of polyvinylamine (PVAm) on polyester (PET) fibers proved to be extremely simple and effective, where at the maximal noble metal capacity as well as the economic basic conditions (operational availability, price, technical feasibility etc.) were taken into consideration. In doing so the finishing of polyester fleeces and needle felts succeeds on semi-industrial level using classical foulard machinery and subsequent thermal fixation (Figure 1). The modification results in modified textiles with extraordinary high polyvinylamine add-ons between 20 and 30 wt.-%., which can be clearly seen in scanning electron microscopy (Figure 2, above). In addition, the established surface amino groups were qualitatively detected by a NH_2-selective color reaction with 2,4,6-Trinitrobenzene sulfonic acid (TNBS) (Figure 2, below). The PVAm-modified material exhibits a strong orange coloring as significant proof for the successful implementation of numerous amino groups, whereas the blank PET substrate shows no coloring. The PVAm-modified textiles were subjected to extensive investigations on the adsorption of noble metals from home-made model waters and various industrial process waters. Figure 3 shows the experimental set-up on lab scale, wherein the noble metal-containing waters can be piped through the textile (once only or circular flow).

Figure 1. Photographs of the used semi-industrial coating plant for the continuous immobilization of polyvinylamine



PET PET-PVAm

Figure 2. Polyester fleece before and after the finishing with polyvinylamine (above: SEM, below: TNBS-Test)

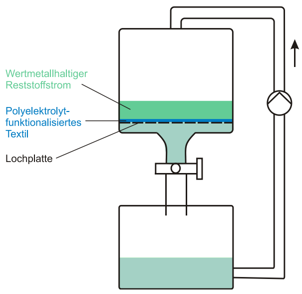


Figure 3. Filtration Set-up (schematic)

The PVAm-modified textile exhibits a high adsorption capacity for platinum (as $PtCl_4^{2-}$ and $PtCl_6^{2-}$), gold (as $Au(CN)_2^-$ and $AuCl_4^-$), silver (as Ag^+ and $Ag(CN)_2^-$) and palladium (as Pd^{2+} and $PdCl_4^{2-}$). In doing so noble metal charging from 10 - 20 mg/g textile were achieved. The binding of the ionic species relies on electrostatic interactions or reversible complex formations. Figure 4 shows schematically the ionic bonding of an anionic palladium species on protonated polyvinylamine under acidic conditions.

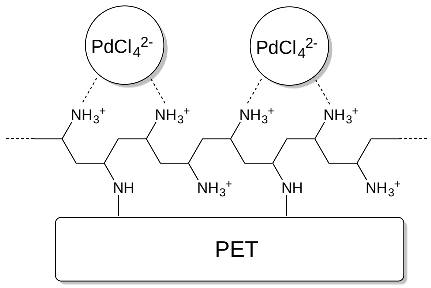


Figure 4. Bonding of metal ions on fiber-fixed PVAm

Simultaneously to the lab investigations the scale-up of the overall process to an industrial level was conducted. Figure 5 shows pictures of the finishing of 500 running meters polyester fleece with technical polyvinylamine (product width 2.20 m, finishing speed 4 m/min).

Figure 5. Finishing PET with PVAm on industrial level

3.2. On-road test for the adsorption of Pd from industrial process waters and metal recovery

During the further procedure it was investigated, whether the on industrial scale produced adsorber textile is able to bind noble metals from real technical process waters. Exemplarily, this was demonstrated on a palladium-containing wastewater from a producer of printed circuit boards. These waters are disposed externally so far. Figure 6 (left) shows a photograph of the corresponding black solution with a palladium content of approximately 400 mg/l. To adsorb the noble metal this solution was piped through the PVAm-modified textile. Figure 6 (right) shows the extremely black colored textile after the successful adsorption of palladium within the filtration set-up. For comparison the picture in the middle shows the blank PET textile after the control experiment. The quantitative metal analysis of the solution by ICP-OES before and after the adsorption yields a reduction of the palladium content of more than 99 % (from formerly 400 mg/l to clearly less than 1 mg/l). After the complementation of all pre-examinations a practice-suitable module for the filtration of palladium-containing process waters on 100 l scale was designed by DTNW. Basically, it consists of a transparent acrylic glass tube, which can be filled with the adsorber textile. The set-up is completed by a filter cap and a suction pump at the bottom, which guarantees a steady flow through the adsorber textile. The on-road test was conducted directly at the manufacturing facilities of the circuit board producer. 200 l of the palladium-containing water (pH level 2, see Figure 6 left) were piped through the textile-filled tube (Figure 7) and each 10 l passage samples of the filtered matter were taken. After the on-road test the textile material was removed for further processing. During the first 100 l occurs an average palladium removal of 75 %. After the passage of 200 l process water the adsorber textile was saturated, no further palladium fixation took place. Simultaneously the concentration charts of other in the water existing metals were determined. Other ubiquitous metal ions such as calcium, magnesium, iron or manganese are not adsorbed by the filter textile. Therefore, they do not disturb the enrichment of the target metal.

Pd-containing process water | PET blank | PET-PVAm

Figure 6. Untreated polyester (middle) and polyester finished with polyvinylamine (right) after adsorption of palladium (left) in the filtration set-up

Figure 7. Operational on-road test for the recovery of palladium from industrial process waters by the use of PVAm-modified PET textiles

The palladium-loaded textile was externally combusted (Figure 8, left) and the elemental metal could be recycled by a subsequent metallurgical processing. Figure 8 (right) shows a picture of the recovered noble metal with a purity of > 99.95 %. In total, approximately 20 g palladium can be generated from 1 kg PVAm-modified textile. So far, the economic overall calculation of the concept is not completed. As a first approximation and in strong dependence from the total process water volume we obtained operational costs for the metal recovery in the range of 1 - 3 EURO/g metal. In the case of palladium this corresponds to 5 - 15 % of the metal price.

4. Conclusion

Natural and synthetic polyelectrolytes are able to fix various metal ions reversibly. We have successfully exploited this capacity and developed a process to bind high amounts of such polyelectrolytes durably on textile materials. The innovative textiles consist of inexpensive and commercially available products and can be produced on an industrial scale by using typical machinery from textile finishing processes. Such textiles are able to adsorb various noble metals, e.g. platinum, gold, silver and palladium, especially from low-concentrated process waters generated by the metalworking industry. The feasibility of the overall-concept was demonstrated successfully for the continuous filtration of palladium-containing process waters generated by a producer of printed circuit boards. In summary, our project results enable the metal-working industry to recover high-value metals even from their low-concentrated process and rinsing waters, where it was impossible or not worthwhile so far. Second, the textile industry was enabled to produce a highly innovative special product with low technical and economic effort. And third, plant manufacturers can plan, construct and operate new filtrations modules for stationary or mobile use at various industries. Besides noble metal recycling, the innovative material opens up widespread applications in the growing fields of strategic metal recovery and environmental protection. Recently, we have started promising investigations on the selective recovery of lanthanum and other rare earth elements metals from large-scale FCC catalyst production for the petroleum refining industry and also on the decontamination of chromate-polluted ground waters and soils.

Pd-containing ash pure palladium

Figure 8. Photographs of different stages of Pd-recovery

Acknowledgement

Based on a decision of the German Bundestag the IGF project "Recovery of noble metals" (grant 17247 N) and the ZIM project "ChromaTex" (grant KF 3047703CJ4) are supported by the Federal Ministry of Economics and Technology (BMWi). The projects "r^4-Lan-Tex" (grant 03X0135C) and "r+Impuls - Edelmetalladsorber (grant 033R153B) are funded by the German Federal Ministry of Education and Research (BMBF). We would like to thank the Institut für Energie- und Umwelttechnik e.V. (IUTA, Duisburg, Germany) for collaboration, in particular Frank Grüning, Christine Kube, Egon Erich and Stefan Haep.

References

Hartinger L. (1991), Handbuch der Abwasser- und Recyclingtechnik für die metallverarbeitende Industrie, Carl-Hanser-Verlag, Munich.

Gräf, R. (1998), Taschenbuch der Abwassertechnik: Umwelttechnik in der Oberflächenveredlung, Fachbuchverlag Leipzig, Leipzig.

N.N. (2007), Aufarbeitung und Rückgewinnung von Edelmetallen, *Galvanotechnik*, 11/2007, 2668- 2672.