

# Preliminary experimental research for silver recovery from radiographic films

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**Abstract.** Global demand for silver remains steadily to about 1,000 million ounces (28349500 kg), of which around 600 million ounces (17009700 kg) are used in industrial applications. Extraction of silver from the ore is expensive and harmful to the environment and low efficiency. X-ray films represent an important worldwide consumer as research on recovery of silver from exposed radiographic films must be oriented to achieve a maximum recovery and a high purity silver, with methods through the by-products will be less polluting for the environment. The paper presents some laboratory tests referring to the recovery of silver from radiographic films by leaching with sodium hydroxide. Two series of experiments were performed with different amounts of used X-ray film.

## 1. Introduction

Silver is a rare earth metal, seen as the symbol Ag, after the Latin word Argentum, which occurs naturally in the environment only as a soft metal, coloured "silver", there are no artificial sources for it. Silver comes from a combination of mining silver, gold, copper, lead, and zinc ore. It also appears as a white powder (silver nitrate and silver chloride), or dark grey to black compounds (sulphide, silver oxide and silver). These compounds are hazardous to the environment. Photography is a sector representing an important source of silver released into the environment.

The mines that produce silver and other metals are another source [1]. Silver is a very inactive metal. It does not react with oxygen in air under normal conditions. However, the sulphur compounds react slowly with air. The product of this reaction is silver sulphide ( $\text{Ag}_2\text{S}$ ), a black compound. Silver does not react with water, acids or many other compounds and it burns only as a silver powder.

Silver has been used due to its functionality and beauty. Silver is a material used both in many industrial sectors and also as a precious metal. As an industrial metal it has thousands of uses due to its remarkable qualities. Silver has the highest electrical and thermal conductivity compared to any other element. Silver bullion stocks dropped steadily, while investments in silver are growing, which is reflected in its relatively constant price. Production will be increased to meet demand. In the last 10 years the price of silver was doubled, currently hovering at about \$ 15 an ounce, but in the same period it also had prices near \$ 50 per ounce [2], as you can see in Figure 1.

The ores that provide silver are limited, so silver mining cannot sustain the consumption. Moreover, the extraction of silver from scrap by products and consumer goods is important to put back into markets that rely on silver [3].





**Figure 1.** Silver price in the last 10 years [2]

## 2. Silver recovery methods from X-ray films

The value of silver hasn't always been compared to that of gold. However, considering the countless uses of silver, gold just does not stack up against silver in terms of functionality. Silver is used in four major areas: industrial, photography, jewellery and manufacture coins. Each year, the photographic sector is allocated about 45% of silver for radiography, which is completely eliminated after use. Despite the fact that many technologies have tried to recover the silver content from this sector, they have not met the environmental demands of less than 5 ppm silver in effluents. In the latest years, to recover silver from the waste generated by the photographic sector are used electrochemical and chemical methods. The ion exchange and electrolytic plating silver units rank as the most acknowledged methods used in most cases. Both methods have been described extensively in the scientific literature, which indicates that electrochemical processes are best suited due to their low operating cost and high recovery rates.

Several authors have done research on the recovery of silver present in effluents generated by the photographic industry. However, information concerning solid waste is not conclusive. Fundamental studies on the subject showed that solutions such as nitric acid, cyanide, ammonia and potassium borohydride are appropriate agents to the dissolution of silver that is found in solid waste from the photographic industry (radiographic films). Besides, it has been shown that it is convenient to use substrates such as stainless steel, titanium, silver, glassy carbon as a working electrode to perform the deposition of silver [4-6]. Moreover, fundamental studies of chemical species in nitrate solid bath generated by waste from radiographic and photographic industry showed that the predominant species in the nitrate is  $\text{Ag}^+$  and hydrogen evolution does not mingle with its deposit [4].

Silver recovery by chemical leaching depends on the heating of the film in the solution of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), nitric acid ( $\text{HNO}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), at boiling temperature for the separation of the inorganic component from the polymer layer. The development of X-ray film leads to waste from the fixer and from the aqueous solutions containing from 1000 to 10,000 mg Ag/L and respectively 50-200 mg Ag/L silver in form of thiosulfate complex [7].

Regarding the data found in specialized literature [8], the following conclusions can be drawn:

a) The easiest way for silver recovery is by treatment with nitric acid. It is an inexpensive reagent, the process is simple and with low consumption;

b) The efficiency by using nitric acid is superior comparing with the using of oxalic acid and sodium hydroxide;

c) Silver recovery rate depends on the density of pulp;

d) The presence of  $\text{NO}_3^-$  ions excess ( $> 30\text{g/L}$  of nitric acid in the solution) had no effect upon improving the silver recovery process;

e) Optimum leaching time was 15 minutes;

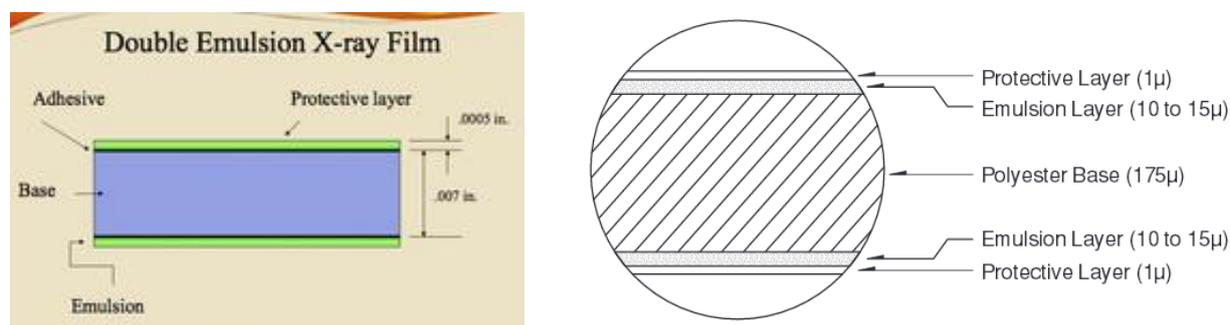
f) There is a strong link between the density of pulp, acid concentration and the leaching time.

In electrolysis a current is applied directly between the two electrodes. The main electrolytic equipment are: one having a rotating movement of the cathode in the solution and the other in which the solution is pumped around an immovable cathode. The silver thus obtained has generally a higher purity than 98%, according to several studies. In spite of that, this method is used only for solutions with high concentrations and it is not capable to reduce silver at a concentration of less than  $100\text{mg/L}$ , considering that the maximum allowed concentration for environmental is  $5\text{mg Ag/L}$  [9]. The raw metal to be refined serves as the anode and the pure metal is deposited on the cathode. A significant experiment for the recovery is by dissolving silver compounds with concentrated nitric acid. It has been used electrolysis with an internal and external steel electrode and a copper electrode at the anode. For extracting silver, enzyme-based methods could be a promising solution since the silver linked gelatine in the emulsion layer may be released using proteolytic enzymes. Thus, research has been directed at the enzymatic hydrolysis of gelatine with *Conidiobolus Coronatus* alkaline protease. After the whole process, the gelatine layer was completely removed, leaving the clean polyester film and silver was recovered by hydrolysis, and thus can be reused both the polyester film and the silver [10].

Worldwide, approximately 57% of the silver present in discarded products is recovered. Concerning the most commonly used metals, silver has the highest percentage of recovery, but large quantities of it are still lost in the different emissions to the environment [11].

Radiographic films consist of a transparent, flexible, blue-tinted base coated on one or both sides with an emulsion, in layers about 0.0005 inch thick – Figure 2.

X-ray film must have different characteristics from photographic film because X-ray exposure is different from light exposure, and it must be manufactured with consistent uniformity and quality as well. Emulsion is a material in which X-ray or light photons from screen interact and transfer information. It consists of gelatine containing microscopic radiation sensitive silver halide crystals, 90-99% silver bromide and 1-10% silver iodide. Furthermore, it also contains several additives like wetting agents, hardener or antifoggants. Gelatine keeps silver halide grains dispersed, prevents from clumping and allows the ingress of processing solutions without affecting the strength or the efficiency, should be pure and porous so that it transmits light and allows chemicals to penetrate to the crystals of silver halide during this procedure. Radiographs are the result of a complex process, as well as the production of emulsion.



**Figure 2.** Radiographic films structure [12]

X-rays strike the grains of the silver halide in the emulsion, so some of the  $\text{Br}^-$  ions are released and captured by the  $\text{Ag}^+$  ions. This modification cannot be observed by common, average physical methods, therefore it is defined as a "latent image". In the presence of the developer, the reduction process is improved and the black, metallic silver, suspended in the gelatine layer, creates an image on both sides of the radiographic film. Radiographic film processing implies complex methods that must

comprise certain rules related to concentration, temperature, time and physical transformations. To obtain high standard X-ray films, a quality control and a superior level of consistency is demanded [13].

Precious metals' price is less affected by the economic destabilization determined by financial crises. This fact can be proved by price-performance ratio reached by the companies involved in the extraction of metals as a raw material. Sustainable development and increasingly severe legislation regarding the environment are making the precious metals recovery, a secure path in conserving natural resources and reducing waste without high costs. Increasing efficiency of recovery methods opens up new opportunities in research field, due to the world demands, decreasing natural resources and human need of development [14].

### 3. Laboratory experiments on recovery of silver from used X-ray

On our own research it was used the silver leaching from X-ray films with NaOH [15]. The exposed X-ray films were provided from Municipal Hospital "Alexandru Grigorescu" Hunedoara. There were conducted two sets of experiments on different amounts of radiographic film.

For the first series of experiments, X-ray film was cut into relatively small pieces, washed with distilled water, alcohol and then dried in an oven at 50°C. The dried film was weighed and placed in a beaker in which was placed a NaOH solution of 1.5M concentration (Figure 3). It was used 100ml of 1.5M NaOH for 50 g of X-ray film. The container was put on the stove at 70°C for the leaching of silver layer. The process was conducted for 1h, with the extraction of the pieces of film, this time with a blue colour (Figure 4).



**Figure 3.** Radiographic film preparation (washing, drying, treatment with NaOH 1.5M)



**Figure 4.** The leaching, the extraction of the clean film, the evaporation of the liquid phase

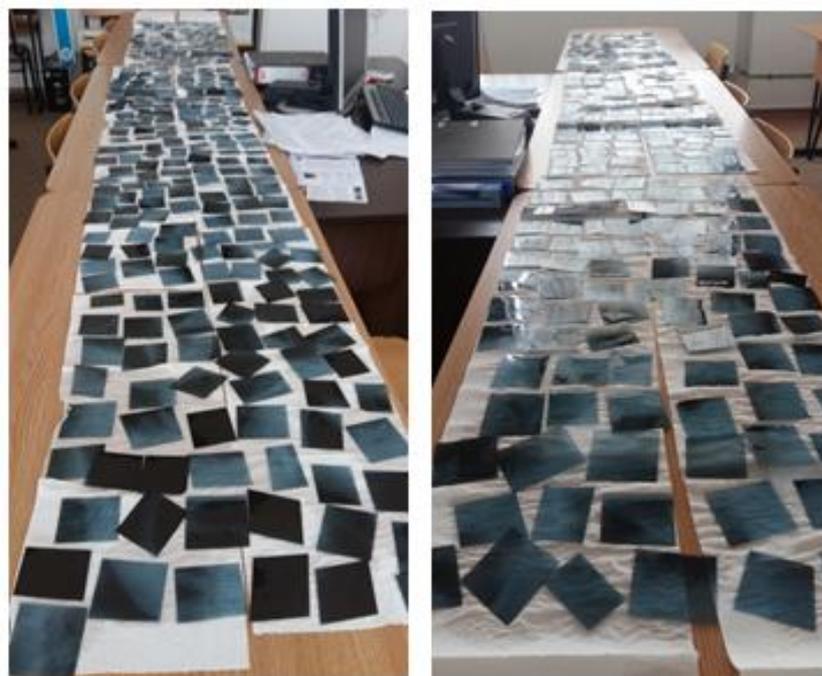
The resulting product was again heated on a hotplate and mixed vigorously until complete evaporation of NaOH; the resulting solid residue was washed with distilled water and then filtered (Figure 5), issues during the experiments being listed below.

For the second series of experiments it was taken a larger amount of developed radiographic film (150g) with 300ml leached with 1.5M NaOH. For this group of experiments the film was cut into larger pieces, washed in distilled water and natural dried in air (24h) on a cotton surface (Figure 6). Thus the drying part in oven was avoided. The same steps as in the first case have been complied for the other parts of the experiments.

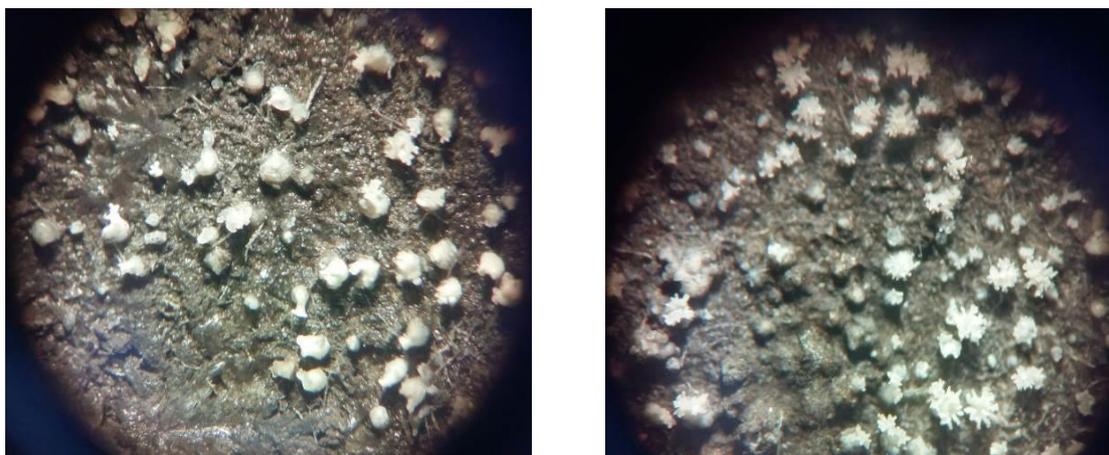
After the drying process of residues, they were analyzed to the stereomicroscope from Metallurgy Laboratory of Physics where it was found the presence of silver grains, and soda crystals which were formed on them – Figure 7.



**Figure 5.** The resulted product, the filtration of the suspension



**Figure 6.** X-ray preparation



**Figure 7.** Stereomicroscope view (x20)

#### 4. Conclusions

After the preliminary experiments carried out for the purpose of recovery of silver by leaching with NaOH from radiographic films the following conclusions were revealed:

- The process comprises a series of steps that must be followed so that it can be recovered at least part of silver deposited onto radiographic film.
- The relatively long duration of the process, which would have in industrial practice would have a rather low economic efficiency.
- Improving the washing of the resulting residue with a larger amount of distilled water until no soda crystals will be found beside the recovered silver.

However, the relatively low results obtained by this method leads to the opportunity to apply a more efficient method for the recovery of silver from X-ray films.

Future research will be directed to radiographs' leaching with nitric and oxalic acid by determining the optimum parameters of leaching. Subsequently, the purification of silver, thus obtained, will be made either by electrolysis or by other methods, less harmful to the environment. In present circumstances, the research for silver recovery is a promising solution for the vast applications of this noble metal.

In PET-film recycling technologies a clear hierarchy is also required. The most important criteria for the recovery of PET-scrap are the degree of "purity" after silver recovery process and the economics of recovery means. Direct reuse in extrusion, for the cleanest PET grade, is the most economical process. The less clean PET samples could be reused after a partial degradation, as by glycolysis, but with higher costs. Film waste represents more contaminated PET. Therefore it must be degraded into the starting monomers, separated then and re-polymerized at the end of the process, which involves further costs. At industrial scale, methanolysis process is more appropriate to be used, while hydrolysis processes, need improving in the future. The only solution for heavily contaminated PET-shreds is they should be incinerated or brought to a landfill. The structure of PET-films must be modify as that they become biodegradable, so the process can be accelerated. Another line of research will focus on recovering Polyethylene terephthalate (PET) after removing the covering film emulsion. [16]

Given the growing number of medical tests worldwide, due to the population growth and the expansion of this type of waste, research on more efficient methods of silver recovery, as well as the PET recovery are appropriate to minimize environmental impact.

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