Use of Aqueous NaOH Solutions to Recover Silver from Radiographic Films

L. Cânda¹*, E Ardelean¹, T Hepuț¹ and M Ardelean¹
¹Politehnica University of Timisoara, Department Engineering and Management, Revolutiei street no.5, Hunedoara, Romania

*Corresponding author: letitia.canda@fih.upt.ro

Abstract. Radiographic films fall into the category of medical waste, and their management is subjected to special regulations. Still widely used in Romania, radiographic films, are subsequently stored in large quantities; at minimum values of 2g Ag recovered per kilogram of radiographic film, a silver recovery of at least 300kg/year is estimated. In the literature, numerous methods of silver recovery from exposed radiographic films have been approached, of which: leaching by sodium hydroxide solution, using reducing agents in a two steps process and silver nitrate cementation with more active metals.

The paper presents the results obtained under laboratory conditions on the recovery of silver using aqueous NaOH solution, running a complete flow of processing, from radiographic films to metallic silver production. There are also presented correlations between the monitored parameters, expressed both analytically and graphically.

1. Introduction
The varying but relatively high content of silver on radiographic films and effluent used in their processing (content ranging from 2–9g / kg, sometimes even higher: 15g / kg) requires its recovery in the context of sustainable development.

In the literature, numerous methods of silver recovery have been approached from exposed radiographic films, of which:

- leaching into sodium hydroxide solution [1,2];
- using of two-step reducing agents [3];
- silver nitrate cementation with more active metals [4,5].

The migration of the emulsion from the radiographic film is a relatively simple process, especially if particular attention is paid to the favorable factors, which are usually: the dissolution temperature, the concentration of the solutions and the speed of rotation if magnetic stirring is used. In recent years, although difficult to achieve, besides recovering silver itself, a particular emphasis has been put on the purity and form of recovered particles.

The starting point of the research was the laboratory production of the highest purity silver from the X-rays films based on the classical and modern methods of recovery or purification, respectively by combining old or new technologies and by making the effectively decisive parameters of these processes. For this purpose, the study of national and world-wide researches has been carried out over time to successfully apply new ways of synthesizing silver [6,7]. Therefore, it was considered research study conducted nationally and globally over time to the successful implementation of new ways of synthesizing silver.
2. Laboratory experiments

In our own research we used radiographic films waste from Municipal Hospital “Alexander Simionescu” Hunedoara, in compliance with legislation relating to privacy, which are kept in the hospital archives.

The basic element of the leaching process is the separation of the inorganic component from the polymeric layer of the radiographic film by leaching with NaOH. Our own preliminary researches [8] have been deepened and expanded through the study of several technological parameters resulting in graphical and analytical correlations.

For quantitative evaluation of leaching phenomenon based on NaOH concentration, aqueous solutions were used to extract silver from the polymer substrate. The film was sequentially treated with NaOH solutions of various concentrations: 1M, 1.25M, 1.5M and 2M respectively – the technological processes diagram A, B, C and D, respectively, as shown in Figure 1, 12 determinations being carried out, each 3 per series. 250g of radiographs were used for each 250g solution. Moreover, laboratory glassware with larger base areas were also used, so that the dimensions at which the film was cut could be larger, 5x5cm² respectively [8].

![Figure 1. The scheme of technological process.](image-url)

To increase leaching speed, the mechanical agitation of the aqueous solution was carried out continuously with a stirring rod. The temperatures at which the silver flow passed into the solution varied between room temperature and 90ºC. The silver colloidal silver solutions containing NaOH were decanted. The residue was washed with distilled water (3–4 times) and then dried. The silver particles were visualized on the stereomicroscope – Figure 2.

To study the equilibrium and the kinetics of the chemical reactions, the concentration of aqueous NaOH solutions was considered for each experiment measuring the leaching time and temperature. As to the rate of agitation, this can be considered a constant factor in the experiments performed, since
mechanical stirring was performed to reduce the leaching time. Figure 3 shows the dependence between the leaching time and temperature at different concentrations of aqueous NaOH [9].

![Figure 2](image2.png)

**Figure 2.** Aspects highlighted by stereomicroscope (20x).

For establishing correlations between the experimental data, they were processed in the Excel (Simple Correlations) and Matlab (Multiple Correlations) programs, the results being presented both in analytical and graphic form [10].

![Figure 3](image3.png)

**Figure 3.** Variation of leaching time depending on the temperature of the solution aqueous NaOH and its concentration
a) polynomial correlations, degree II; b) polynomial correlations, degree III; c) polynomial correlations, degree IV; d) correlations, power function.
3. Interpretation of results

Regarding the simple correlations, these are expressed by II, III and IV degree polynomial functions as well as the power function (Figure 3). Considering the values for the correlation coefficient, it can be considered that, regardless of the type of correlation, they are representative. Increasing the temperature of the solution leads to a decrease in the leaching time, which is intense within the temperature limits of 20–60°C for the 1M concentration solutions, the time decreasing from 40 min to 5 min. For solution solutions of 1.25M; 1.5M and 2M respectively decrease in time is intense in the temperature range of 20–40°C, the reduction of time being from 20 to 10 min. At temperatures above 60°C, it can be considered that the reduction of the leaching interval is insignificant. It can be also considered that an optimal leaching time is obtained at temperatures above 60°C and is of technological interest the average value obtained by applying the four correlations.

Furthermore, the graphical dependencies of Figure 3 show that an increase in the concentration of the solution from 1M to at least 1.25M results in a significant decrease in the silver transition time of 80–90°C, thus increasing the concentration to 2M or above is not justified (both for economic and environmental reasons). The minimum leaching time at 80–90°C takes place at a concentration of 1.5M.

Referring to double correlations performed in the Matlab calculation program, we considered the temperature of the aqueous solution of NaOH ($T_{\text{NaOH}}$) and its concentration ($c_{\text{NaOH}}$), as independent parameters, and as a dependent parameter: the leaching time ($t_l$), correlations shown in Figure 4 [10].

![Figure 4](image_url)

**Figure 4.** Dependence of leaching time on the temperature and molar concentration of the solution

The multiple regression equation is given by relation (1), the correlation coefficient being $R^2 = 0.954$.

$$t_l = 0.009 \cdot T_{\text{NaOH}}^2 + 16.6 \cdot c_{\text{NaOH}}^2 + 0.329 \cdot T_{\text{NaOH}} \cdot c_{\text{NaOH}} - 1.862 \cdot T_{\text{NaOH}} - 77.954 \cdot c_{\text{NaOH}} + 126.312 \quad (1)$$
Figure 4 shows the correlation surface, the plane projection of the level curves, the leaching time variation subdomains and the spatial projection curves respectively. Knowing the values for the level curves in the plane projection or the subdomains allows, for any temperature and concentration, the graphical determination of the leaching time, or the matching of the desired leaching time, respectively, the values of the independent parameters can be determined. For example, we consider point A (35, 1.5, 15) – Figure 4. Increasing the temperature to 50°C while maintaining the constant concentration leads to a decrease of the leaching time to 5min (i.e. by 0.66min/°C) – the point B (50, 1.3, 5) respectively. The reduction of the leaching time can also be achieved by increasing the concentration of the leaching solution; an increase of 0.2M at the same temperature determines leaching times of 11min – point C(35, 1.5, 11), thus 20min/mole solution. A simultaneous increase of the two independent parameters: temperature or molar concentration of the solution, also leads to a decrease of the leaching time. Thus, starting at point A (35, 1.5, 15) at point D (50, 1.5, 2.5) a decrease of the leaching time is obtained from 15min to 2.5min i.e. 0.83min/°C or 62.5 min/mole solution.

After complete drying in the oven, the residue was introduced into a ceramic crucible, covered with an amount of about 30 g of borax and introduced into a silicon bar furnace, in which the thermal regime of fig.5 has been respected. Cooling of the crucible was done with the oven, to avoid thermal stresses in the ceramic crucible. At extraction of the crucible from the furnace pieces of silver metal caught in a glass borax table could be seen – “borax pearl” – Figure 6. The recovery of the pieces of silver – Figure 7 was done after the crucible was reheated in the presence of water which favored the decomposition of the borax mass, the working temperature in this case being 100–150°C.

**4. Conclusions**

As a result of the experimental approach to the leaching of radiographic films with aqueous NaOH, the following conclusions were drawn:
The optimal working concentration of the aqueous NaOH solution is 1.5M – technological variant B, which was maintained constant by supplementing it with distilled water quantity to ensure the same volume of the leaching vessel;
The leaching process was initiated at the ambient temperature of the laboratory and the working temperature ranged between 65–90°C;
The length of the leaching process varied between 40–50min for each technological variant;
The total residue resulting from the complete evaporation of the aqueous solution was 16.21g;
The amount of silver resulted after melting the residue in the furnace in the presence of borax was 6.54g;
The washing steps (especially the use of distilled water) and the drying of the films (natural or even more in the oven), which leads to a reduction of the processing time and economic efficiency of the process (reduction of water costs and energy), are no longer necessary;
For economic reasons, the use of current water was used in the process of silver solution transfer from radiographic films, as well as the washing of the filtrate instead of the double distilled or triple distillate, with the same efficiency of the process;
Recycling of the polymer support on the plastic circuit was also considered, concurrently with the recycling of the residual solution in the recovery process, to avoid pollution of the ecosystem to final disposal.

5. References
[1] Marincovic J, Korac M, Kamperovic Z and Matic I 2006 Acta Metalurgica Slovaca 12 pp 262–268
[2] Nakiboğlu N, Toscali D and Nişli G 2003 Turkish Journal of Chemistry 27(1) pp 127–133
[3] Shankar S, More SV, Seeta Laxman R 2010 Kathmandu University Journal Of Science, Engineering And Technology 6(1) pp 60–69
[4] Jaskuła M 2009 Jordan Journal of Earth an Environmental Sciences 2(1) pp 84–95
[5] Aktas S, Morcali MH and Yucel O 2010 Canadian Mettalurgical Quarterly 49(2) pp 147–154
[6] Li G, He D, Qian Y, Guan B, Gao S, Cui Y, Yokoyama K and Li W 2012 F Int J Mol Sci. 13(1) pp 466–476
[7] https://www.google.com/patents/US6290749 – Preparation of ultra–pure silver metal US 6290749 B1
[8] Cânda L, Hepuţ T, Ardelean E 2017 IOP Conference Series: Materials Science and Engineering 106 pp 1–9
[9] Cânda L, Ardelean E, Hepuţ T 2018 IOP Conference Series: Materials Science and Engineering 294 pp 1–8
[10] Cânda L Research on the recovery of silver from radiographic films and effluents – PhD Thesis 2018 University Politehnica Timișoara