SUMMARY
of the doctoral thesis "Research on the recovery of silver from radiographic films and effluents"

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Introduction

The study of silver recovery techniques from radiographic films and effluent involves: researching current processes, forecasting the amount of waste (radiographs and solutions) generated locally for a specified period (one quarter), efficient management and recording of data from radiographic films, collecting and processing them in order to optimize silver recovery processes through various technologies. The research objectives are:

- increasing the efficiency of silver recovery;
- reduction of costs and recovery time;
- mitigating the impact of these wastes and the resulting solutions on the environment [1/2].

World production of silver is currently insufficient to meet demand, growing about 2-2.5% per year. Currently, 94-98% of radiographic films are used in medical services. Radiographs may contain between 5-15g Ag/kg of film, representing a significant secondary source of silver [2/8].

The experimental researches and the processing of the obtained data were carried out in the laboratories of the Hunedoara Engineering Faculty, and the radiographs were provided by the Municipal Hospital "Alexandru Simionescu", Hunedoara (archive). From the experiments carried out, and the cost, efficiency and recovery calculations, it can be concluded that effective silver recovery can be achieved from exposed X-ray films, with profit being spent on improving medical services in the radiology department.

CHAPTER 1. TECHNICAL CONSIDERATIONS FOR PRECIOUS

Any used equipment containing precious metals is a valuable secondary material, but sometimes also a source of environmentally harmful substances. The demand for electrical and electronic equipment (EEE), as well as the number of devices and devices involving the use of precious metals in the manufacturing process, has increased considerably with technological advances. Medical investigations, through related technology, constitute a significant consumption of precious metals. Innovations on electrical and electronic technologies in all areas of activity have reduced their lifecycle, thus increasing the generation of waste containing precious metals. A three-pillar strategy is therefore needed: waste prevention, recycling and re-use, minimizing environmental impacts and promoting the efficient use of wasted resources [3/18].

Over the last decade, many countries have issued legislation on the management of non-ferrous metal waste. Underground storage of e-waste or burning in incinerators is no longer allowed without the isolation of hazardous materials. Moreover, the export of e-waste to underdeveloped countries is not allowed under international regulations [4/21].

E-wastes are classified as hazardous materials, therefore they should be managed properly. Moreover, the presence of precious metals (PMS) in e-waste such as gold (Au), silver (Ag), platinum (Pt), gallium (Ga), palladium (Pd) (Te), germanium (Ge) and selenium (Se) make them attractive for recycling.

Regarding the recovery of silver, it is of interest to recover it from radiographs and effluents, and for platinum, the main sources of recovery are spent catalytic converters.

CHAPTER 2. METALURGICAL PROCESSES USED FOR THE EXTRACTION OF PRECIOUS METALS

Precious metals are among the few materials that do not degrade and do not lose their chemical or physical properties in the recycling process. Consequently, they have the ability to be recycled by an infinite number of times. Precious metals are used in a wide range of applications, not only in electronic and communications equipment, spacecraft and reaction aircraft engines, but also in mobile phones or catalytic converters. The most frequently recovered precious metals are gold, silver and platinum group metals.

Interest in gold recovery is due to its vast industrial applications, high market prices, and value attributable to the international economic crisis and political as a limited resource.

Recycling involves two steps, by generating the first metal concentrate by mechanical enrichment (pre-treatment), followed by the pyrometallurgical/ hydrometallurgical processing of the concentrate. Compared to the pyrometallurgical method, the hydrometallurgical process being more accurate, predictable and easy to control. Leaching is the first step for recovering gold using the hydrometallurgical process. Cyanide gold leaching has been the most common method for over a hundred years because of simplicity and cost, and the efficiency of the process. However, the toxicity and safe disposal of cyanide in the environment raises the need to develop other leaching agents. Alternative substances such as thiourea, thiosulfate or thiocyanate have recently been proposed as non-cyanide leaching agents.

For the gold recovery from different types of leach solutions, different methods are used, such as cementation, adsorption, solvent extraction, ion exchange, etc.

Platinum is a key element in the manufacture of catalytic converters. The catalytic converter is a device used to reduce the toxicity of emissions from internal combustion engines. Spent catalysts can be subjected to refining in order to recover metals such as nickel, cobalt, molybdenum, vanadium [5/54, 6/55].

A typically catalytic converter contains a total of 1.5 grams of platinum and 4 grams of other metals of the same group. The exact amount of platinum varies, depending on the applied manufacturing technology. However, this quantity is high compared to the primary resource yield. Recycling of spent catalysts is done more frequently by pyrometallurgical methods.

Silver naturally appears in the environment as a "silver" soft metal, and there are no artificial sources for it. Photographic materials are the major source of silver-containing waste that is released into the environment.

Recovery of silver from waste in the form of solutions, such as those produced by the classical medical and industrial processing of X-ray films, photographic films and images, has been practiced for over 100 years. However, the economic viability of the process has changed radically in recent years.

Modern recovery methods offer the ability to achieve rapid depreciation, which means faster profits.

Studies and researches at national level on the recovery of silver from radiographs are not deepened. At international level, studies over time on the recovery of silver from radiographic film waste have revealed two typical methods: pyrometallurgical processes, hydrometallurgical processes or by acid leaching.

Following the study on the recycling of precious metals by various methods from different wastes worldwide, the following conclusions can be drawn:

- **Collection of waste containing precious metals** is a decisive step for efficient recycling and efficient management of resources.
- **Pre-processing steps**, including sorting, dismantling, crushing and releasing, will insulate metals, alloys and other materials from a complex e-waste material.
- **Unaccomplished knowledge of the methods underlying melting and refining processes** is another barrier that affects the recyclability potential of precious metals.

CHAPTER 3. THE DEMAND FOR THE RECOVERY OF SILVER FROM RADIOGRAPHIC FILMS

Radiographic films, photosensitive, are cellulose nitrate brackets provided with a silver halide film on both sides. The X-ray film contains an average of 7.5g Ag / kg, while the negatives are 9g Ag / kg and 2g Ag / kg camera films. The amount of silver in the fixation solution depends on the mode of processing, but the average is 3g / l.

Waste management, including the recovery, is based on multiple impact activities:

- technologically, by using waste in production streams, thus replacing raw materials in many cases;
- economically, by reducing manufacturing costs, often waste requiring minimal processing operations before being reintroduced into the technological process;
- socially, by creating new jobs where waste is needed in a more useful form for the technological process;
- ecologically, by removing waste already produced and stored but posing a threat to the entire ecosystem, which are very rarely inert.

Recovery of silver from radiographs is a perspective solution with an increased potential for the future.

The development of the centers for the recovery and recycling of radiographs in Romania would lead to a considerable decrease of the expenses for the exploitation and import of silver as well as the increase of the national reserves of silver, metal with special properties and with extensive use.

CHAPTER 4. THEORETICAL ASPECTS OF SYNTHESIS AND RECOVERY OF SILVER FROM RADIOGRAPHIC FILMS

The research of silver recovery from radiographs has been oriented over several directions over time. Pyrometallurgical methods applied are considered obsolete and is energy intensive. Studies on the recovery of silver by enzymatic methods are in a relatively incipient phase, with ineffective results, assuming a long timeframe for separating the emulsion film from the film [7/1].

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

- leaching into sodium hydroxide solution [8/11,9/12];
- the use of two-step reducing agents [10/93];
- silver nitrate cementation with more active metals [1/2,11/94].

Nanoparticles (NP) have a wide range of applications in areas such as cosmetics, food and feed, environmental health, mechanics, optics, biomedical sciences, chemical industry, electronics, space industries, light transmitters, nonlinear optical devices and applications photoelectrochemical.

For the synthesis of silver nanoparticles, various methods are used, for example chemical ones, including chemical reduction, using one or more organic and inorganic reducing agents, electrochemical techniques, physico-chemical reduction, radiolysis, laser ablation, microwave irradiation, or sonoelectrochemical reduction or sonochemical [12/99,13/100].

Silver has been successfully recovered from photographic films using a solution of NaOH without any separation or purification. Since colloidal solutions could not be filtered, granular and shiny metallic silver was obtained with a purity level of 99.24% ± 0.03 [9/12].

The cementation process is used for the synthesis of precious metals from leaching solutions and for the purification of electrolytic solutions. Metal replacement, also called cementation, is based on the use of metals such as iron, zinc and copper, which are more active than silver for efficient effluent recovery. The process is generally composed of two reactions:

- reducing the more active metal ion;
- oxidation of the less active metal.

To synthesize a pure silver powder, the cementation process can be applied by precipitating the silver compound from a solution, followed by the precipitation reduction, and then for increasing the apparent density, the cement is heated in a furnace, preserving its morphology.

The study of a vast material of methods of synthesis and recovery of precious metals and especially of silver, was the basis of the laboratory research for the recovery of silver from the X-rays.

CHAPTER 5. OWN RESEARCH AND EXPERIMENTS ON SYNTHESIS AND RECOVERY OF SILVER FROM RADIOGRAPHIC FILMS AND EFFLUENTS

In my own research there were used X-ray film waste from the Municipal Hospital "Alexandru Simionescu" Hunedoara, in compliance with the legislation on data confidentiality. According to the information provided, every month 2500 radiographs are processed on average. Radiographs have an average mass of 20g, which means that the mass of radiographs developed monthly is about 50kg. One kilogram of radiographs contains at least 2g of silver, so silver that could be recovered is at least 1kg per year, in a single hospital unit of medium size and capacity. By extrapolating these data at national level, a minimum of 300kg of silver per year could be obtained from the use of exposed X-ray films.

In the experiments performed, several methods were used to recover the silver, the most eloquent being:

- with sodium hydroxide solution at various concentrations, including using reducing agents;
- cementing of silver with more active metals (copper, iron, zinc) from silver nitrate solutions obtained by percolation of photographic emulsion in nitric acid.

The first experimental approach involved the leaching (percolation) of the film into NaOH solutions. In this case a number of 7 series of experiments were performed on different quantities of radiographic film waste, modifying experimental parameters: concentration of NaOH solution, film drying mode, leaching temperature, residue separation mode, etc. As a result of the experimental research, a simplified technological variant, generically called the B-E scheme, presented in fig. 1/5.14. The resulting residues were analyzed/visualized before melting, in fig. 2/5.18 showing both the silver particles and the existing impurities. After melting, the pieces of silver, which are shown in fig. 3/5.21.

Experiments resulted in the following conclusions:

- The process involves a series of steps to be followed so that the silver deposited on the developed radiographic film can be recovered at least partially.
- The length of the process is relatively high, which in industrial practice would lead to lower economic efficiency.
- Eliminating the need to wash the resulting residue (with relatively large amounts of distilled water to remove the soda crystals on the recovered silver). This avoids environmental pollution by evacuating liquid residues from the washing process.
- As regards the leaching of the radiographic films in NaOH aqueous solution, it is recommended that the following process parameters: concentration of 1.5 M NaOH aqueous solution, the process range of 80-90 °C.

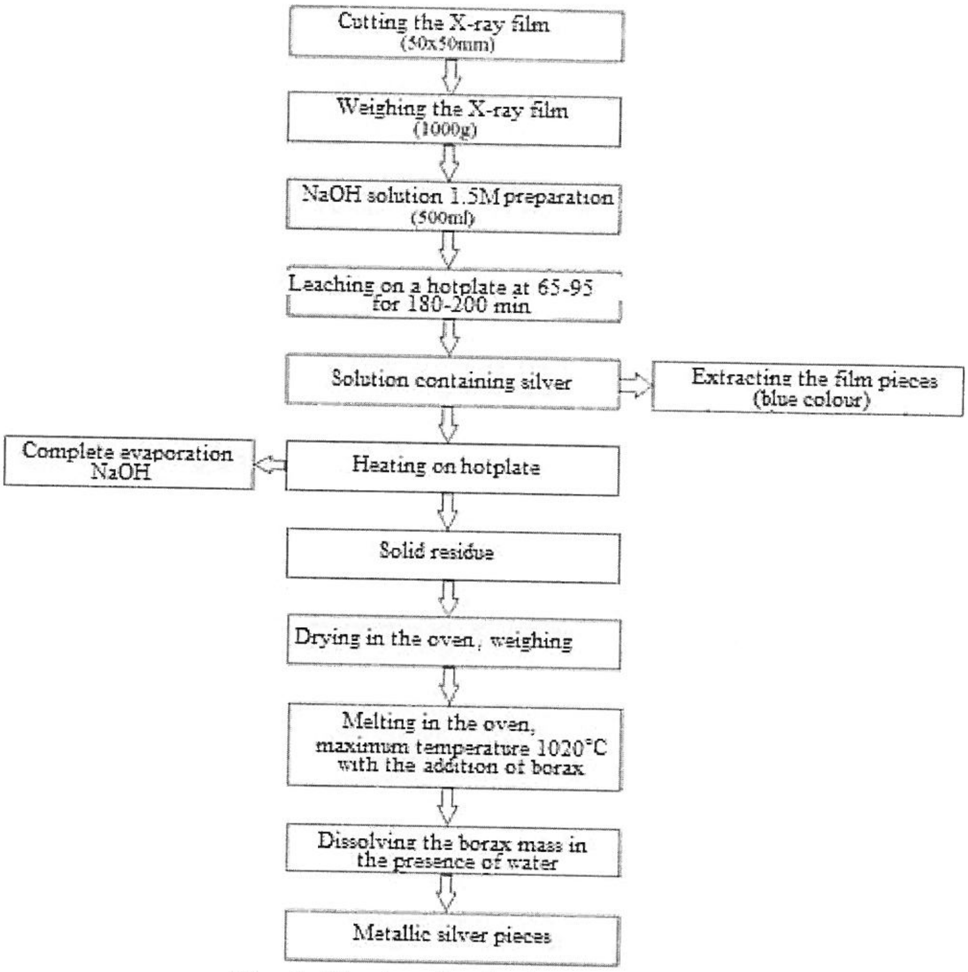

Fig.1. Technological variant B-E

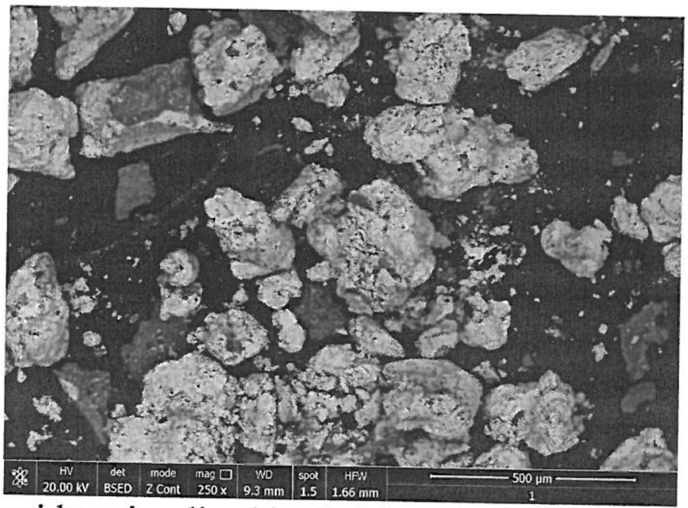

Fig.2. The solid residue visualized by SEM analysis (magnification order x250)

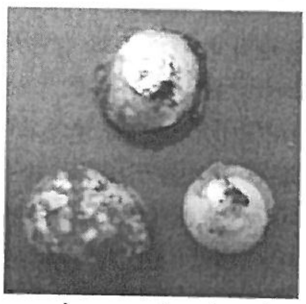

Fig.3. Silver pieces obtained with NaOH

The solutions containing silver react with nitric acid if its concentrations are sufficiently high. The reaction results in silver nitrate and other chemical compounds depending on the type of solution and in some cases the silver can be recovered from the mixture either by chemical reduction with one or more reducing agents or by cementation, a method used in the purification of silver.

The second line of research consisted of cementation of silver from silver nitrate, silver resulting from the passage of the nitric acid solution of silver on the radiographic film. Cementing of silver was carried out in three variants, using Cu, Zn and Fe, but in the case of Zn and Fe, no the silver particles could be seen after filtration.

The experimental approach included a series of 7 series, based on the obtained results, reaching a technological variant considered optimal, called the scheme R - presented in fig.4/5.59.

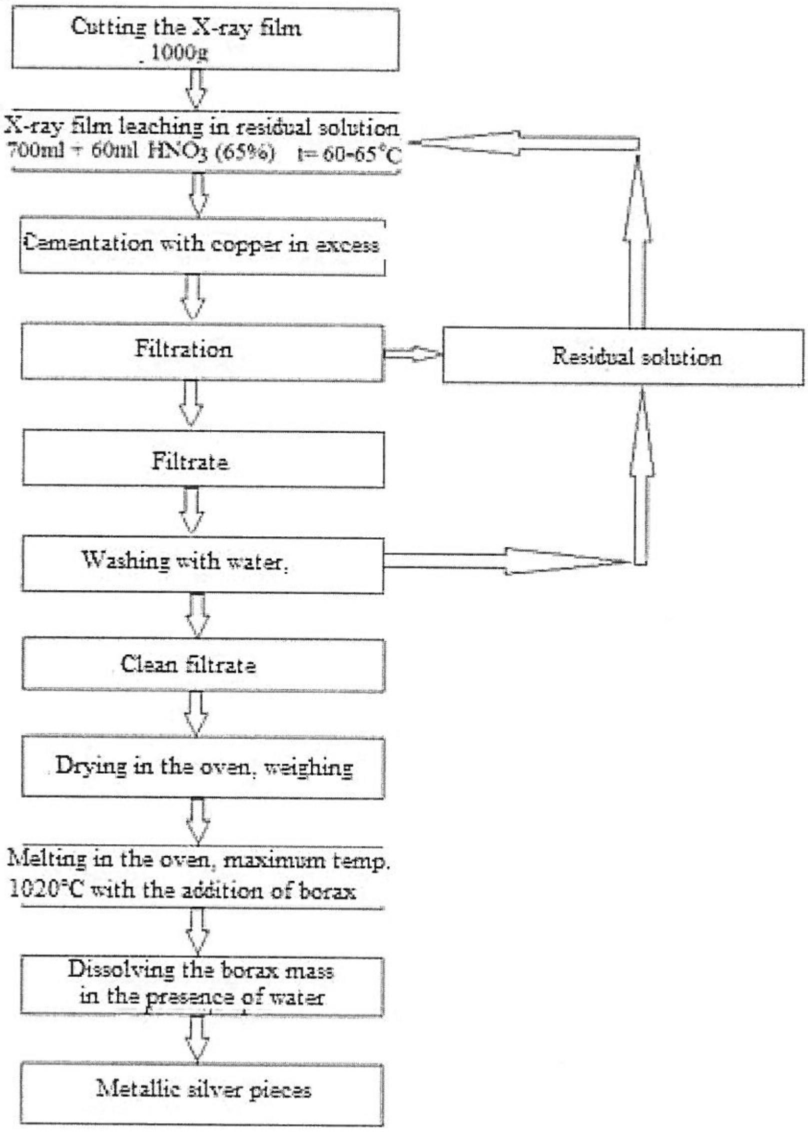

Fig.4. Technological variant R

The analyzed samples were analyzed both by stereographic and electronic scanning microscopy, the visualized aspects being presented in fig.5/5.55 respectively fig.6/5.57.

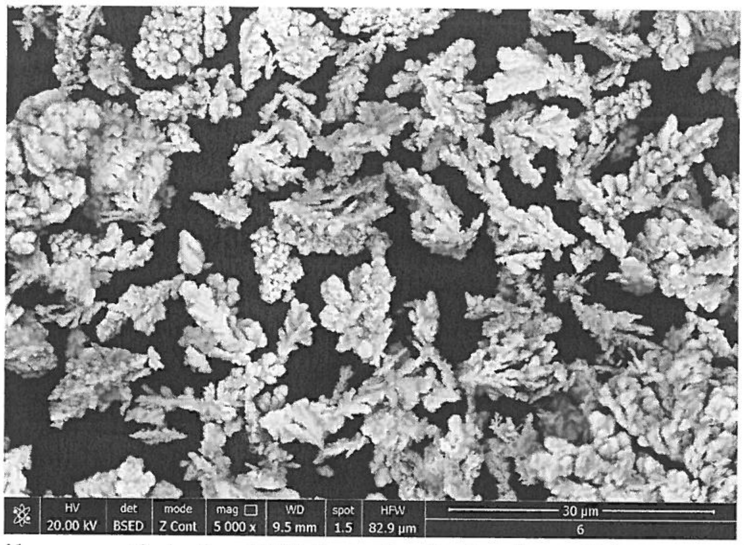

Fig.5. Viewing silver particle by SEM analysis (order of the magnification X5000)

Fig.6. Silver with dendritic aspect (x20)

Following the silver-based study of exposed radiographs using nitric acid, the following conclusions are reached:

- The optimal stripping temperature is 55-65°C, which leads to a percolation time of radiographic films of approx. 30s.
- The optimum nitric acid concentration in the aqueous solution is 20% (higher values resulting in higher cost price of the process, and lower values in increasing the stripping time of the silver from the radiographic emulsion, respectively the decrease of the process yield).
- The optimal recommended dilution ratio before cementation is 1:1.
- The shape and dimensions of the obtained silver particles differ for each stage of cementation, at first the particles are of smaller size, later they grow and can be visualized with the naked eye.
- The idea of perpetual reuse of solutions in the following processes, without being dispersed in the environment, makes this new method a possibility of large scale application for the recovery of silver from the radiographs, finding one of the main deficiencies of the hydrometallurgical methods.
- When the concentration of copper in the solution reaches a too high concentration, it can be subjected to an electrolysis process with copper anode, a classic method of copper recovery and refining. Considering that this happens after

a large number of re-use, and the amount of solution is not high because it evaporates, the costs of this remediation process are low.

- The purity proven by the results of laboratory tests shows that silver recovery through cementation is a viable method of recovering it from radiographs.

CHAPTER 6. COMPUTERIZED MANAGEMENT SYSTEM FOR X-RAY FILMS

The implementation of a digitization and organization of hospital records together with the installation of a dynamic and comprehensive information retrieval system should be a priority for any medical office / hospital unit to improve medical services.

In this chapter a computer application was developed, aiming at accurate record of the management of radiographs in a hospital, which would allow for the retention of radiographic films at the source, with the possibility of centralized storage and subsequent delivery to the companies specialized in the recovery of silver.

The development environment chosen to build the application is Microsoft Access [14-16/152-154]. The application is Windows Forms, allowing a user-friendly interface to perform all patient management operations in a graphical way that can be easily understood by any user with minimal computer knowledge.

Starting from this application, which allows the organization of patients and radiographies in a database, a complex network can be created that includes all medical offices / hospital units that keep a record of radiographs. Such a network would greatly simplify the components of integrated radiographic film management (organizing x-ray storage, storage conditions as well as handing over to processing firms to recover silver) as well as searching and accessing radiographs regardless of time and location.

CHAPTER 7. FINAL CONCLUSIONS. ORIGINAL CONTRIBUTIONS. DIRECTIONS FOR FURTHER RESEARCH

Among the final conclusions highlighted in the PhD thesis, the most significant are presented below:

1/3. Studies on the recovery of precious metals are a concern of scientists, supported by institutions and firms in the global economic context.

2/5. The recovery rate of precious metals is still quite low, but current research can provide better prospects for both waste management and clear, concrete ways and with increased efficiency for their separation and re-use.

3/12. Recovery of silver from radiographs is of particular importance due to their extensive use in many fields, including medicine.

4/18. One of the research directions consisted in the use of aqueous sodium hydroxide solution as an inorganic film leaching agent deposited on the polymer layer (process A). From the basic version, with some modifications, 9 variants were detached, showing both the technological flows that were passed and the aspects during the experiments.

5/19. Based on data and observations from laboratory experiments correlated with mathematical processing results (graphically and analytically expressed in Excel and Matlab computations), optimal variation ranges were obtained for the influence parameters considered significant: the concentration of the aqueous solution of NaOH 1.5M, leaching temperature 80-90°C.

6/20. From this research direction, a simplified optimal variant (technological scheme B-E) has been reached.

7/21. The second direction of research under laboratory conditions consisted in the stripping of the inorganic silver-containing film of an aqueous solution of nitric acid, followed by the cementation of silver with electropositive metals and 7 different technological variants.

8/23. The influence parameters identified in the simplified optimized version (technological scheme R) were as follows: the stripping temperature of 55-65 ° C, the concentration of aqueous HNO3 solution of 20%, the use of copper in the cementation process (obtaining yields of higher silver than the use of iron or zinc), the need to dilute the resulting solution after percolation in order to reduce copper consumption.

9/24. The purity of the silver obtained from the technological scheme R was high, which led to the elimination of the subsequent refining step of the silver.

10/25. The database provides a record (by scanning) of patient radiographs, storing them for each patient so that they can be accessed by specialists, regardless of the date or location, the source (generator) capture of the X-rays a period clearly defined by internal rules).

The most significant original contributions are as follows:

1/3. Establishing, based on the experimental data from the literature, some simple correlations (in the Excel calculation program) - graphically and analytically expressed by higher-level polynomial functions, and double correlations (in the Matlab calculation program) - graphically expressed through correlation surfaces, level curves in plan and space projection as well as the representation of subdomains of variation) and analytical (by polynomial equations of degree 2, grade 5 and composite equations - polynomial + logarithmic), in all cases being presented, correlation coefficients obtained.

2/4. The use of such graphical representations and / or analytical equations is of interest for industrial practice in order to determine some variation parameters, optimal framing domains and the time allocated to the quantitative and qualitative determinations of the processes.

3/5. Establishing a simplified working method for recovering silver from radiographic films using an aqueous solution of sodium hydroxide (the BE technological scheme), based on the numerous experiments in the laboratory and the processing of data obtained in the Excel and Matlab computing programs, and optimal working parameters, respectively.

4/6. Following the experimental approach to the use of NaOH in radiographic film leaching, it was concluded that the washing step (especially with the use of distilled water) and drying of the films (natural or even more which reduces the processing time and the economic efficiency of the process (reducing water and energy costs).

5/7. The experimental choice of copper as a metal used for cementing silver in silver nitrate solutions.

6/8. Establishing a simplified working method for the recovery of silver from radiographic films using an aqueous nitric acid solution (R-scheme) based on the numerous laboratory experiments and the processing of data obtained in the Excel and Matlab computing programs, and respectively optimal working parameters.

7/9. The use of current water in the process of transferring silver from the radiographic films as well as washing the filtrate instead of the doubled or distilled trip, for economic reasons.

8/10. Copper recovery from residual solutions by electrolysis and reuse of all by-products.

9/11. The metallic silver obtained by treating the films with nitric acid, after melting in the oven, has a very high purity of over 99%.

10/13. In the whole experimental approach, it was assumed that the protection of the environment and the reduction of the pollution level is a priority.

11/14. Creating a database, which can be applied at regional or even national level, which allows for the proper management of X-ray films at source (medical offices / hospital units), while allowing easy access for doctors, patients and network administrators and ensuring better medical performance, while respecting the confidentiality of patient data.

Considering the results obtained through the elaboration of the Ph.D. thesis entitled *"Researches regarding the recovery of silver from radiographic films and effluents "*, I consider that they are of interest for the recovery of silver from radiographs at industrial level, and future research in the field can address the following directions:

- Technological transfer to an interested industrial processor;
- Expanding research by recovering silver from effluents (revelator and fixer);
- Expanding research by recovering silver, gold and other precious metals from WEEE, catalysts and other waste containing precious metals [17/155, 18/151];
- Pilot implementation of the database on the management of the exposed radiographic films with minimal environmental impact.

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