Reducing UPOPs and Mercury Releases from The Health Sector in Africa

Module 12

Management of Photochemical waste

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25 years gef GLOBAL ENVIRONMENT FACILITY
INVESTING IN OUR PLANET

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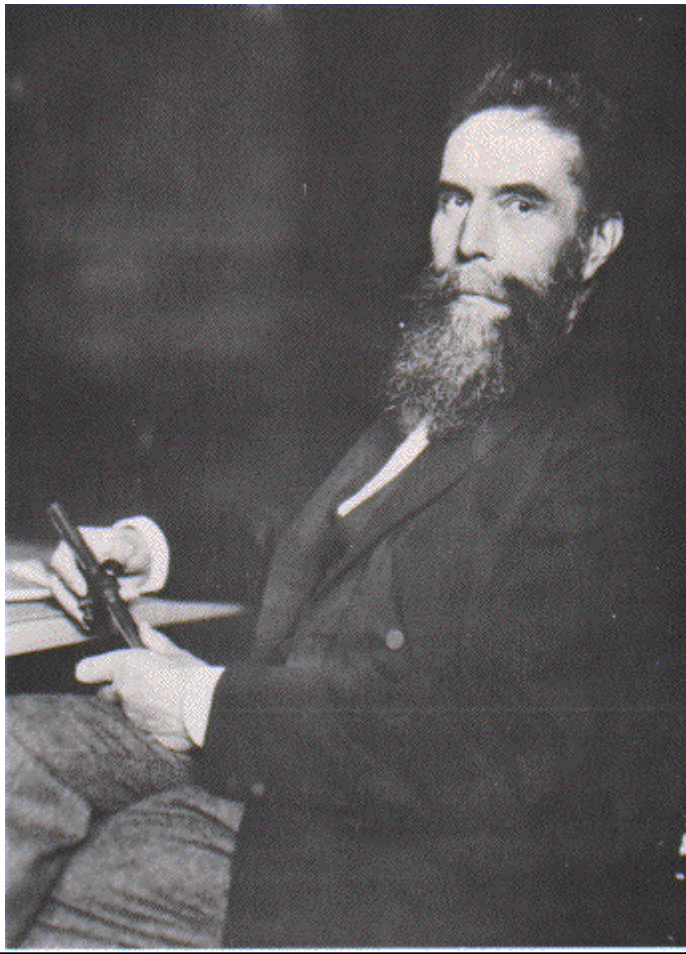
In The Beginning …

- On 8 November 1895, William Conrad Roentgen discovered the x-ray.



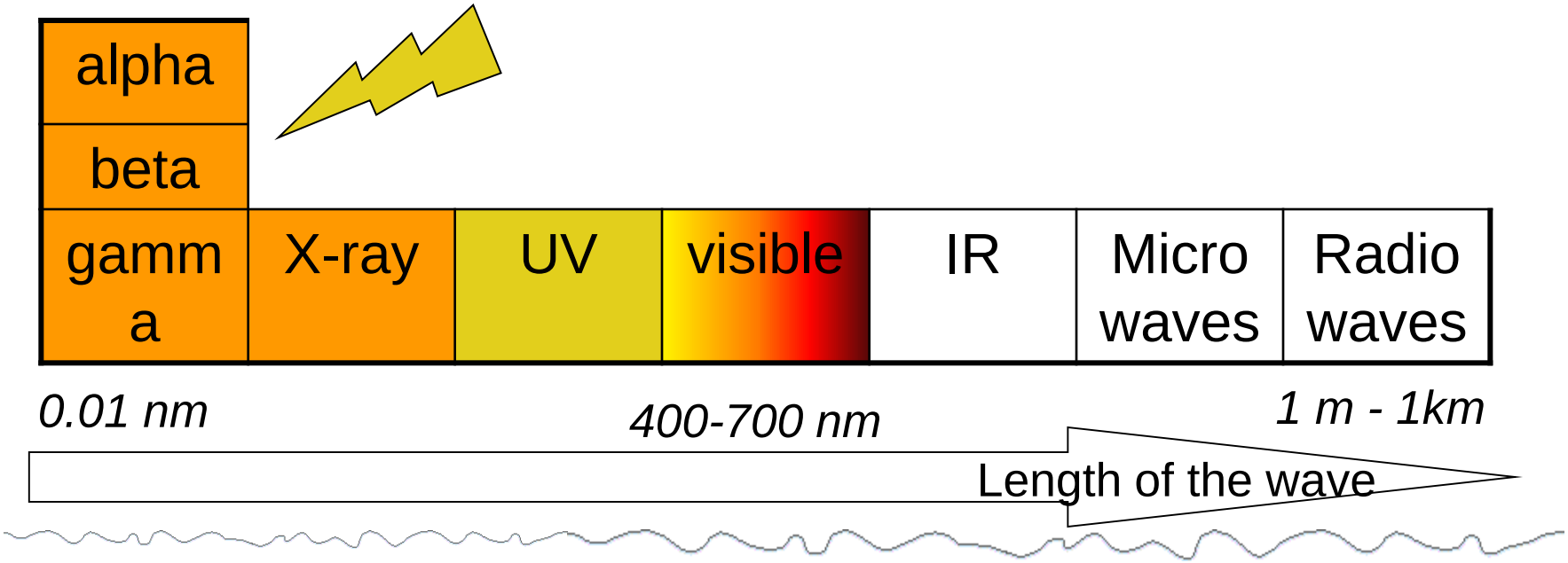
The First X-Ray

On 22 December 1895, Mr. Roentgen made the first x-ray photograph (From Mrs. Roentgen's hand).

The Aftermath

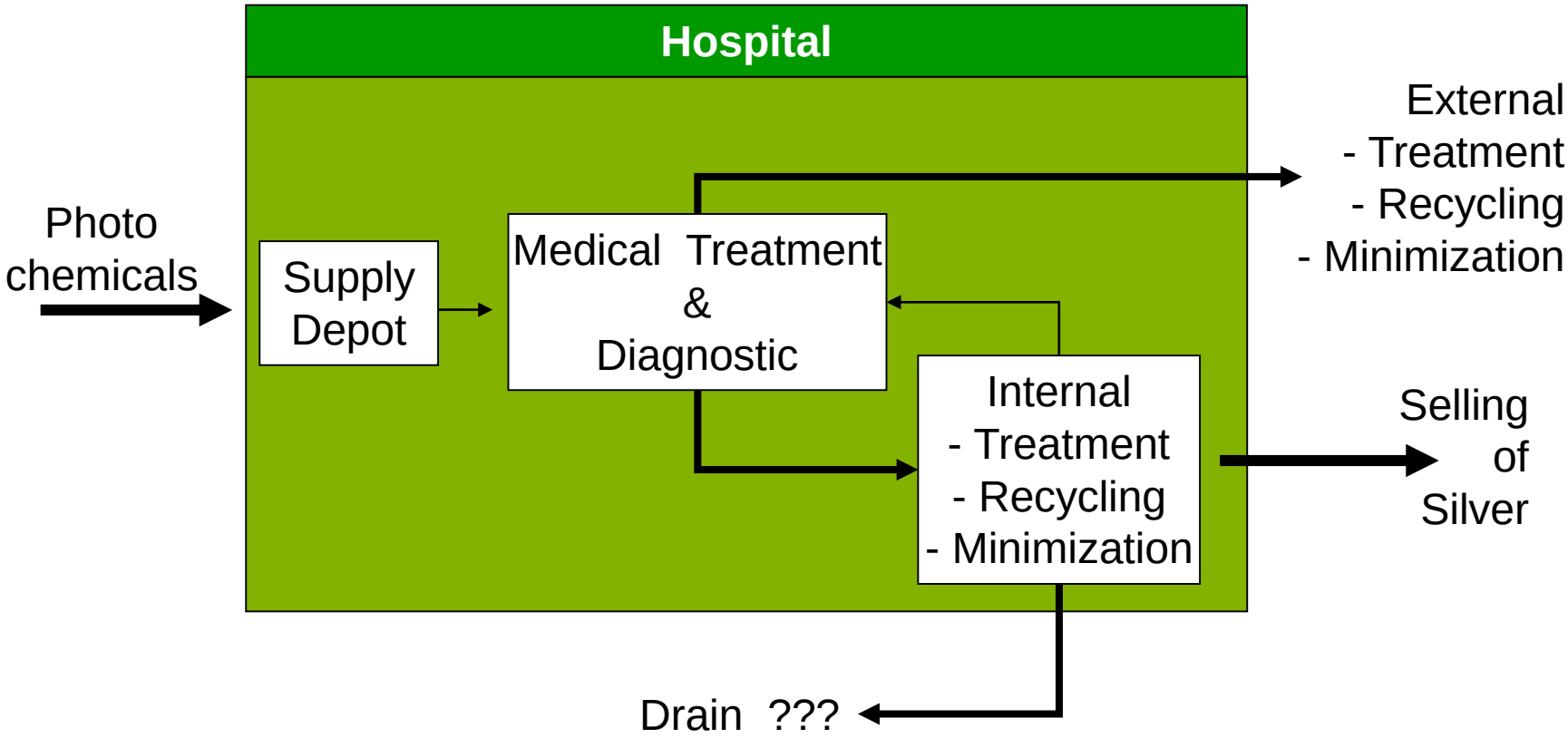
- On 1 January 1896, Roentgen announced his discovery to the world.
- 14 February 1896, four days after news of the discovery reached the U.S, x-rays were used to guide surgery in New York.
- In early 1896, the Italian military began using x-rays to diagnose and treat wounded soldiers.
- Today, after more than 110 years, radiology is one of the main diagnostic tools in the healthcare sector.

Kinds of Radiation

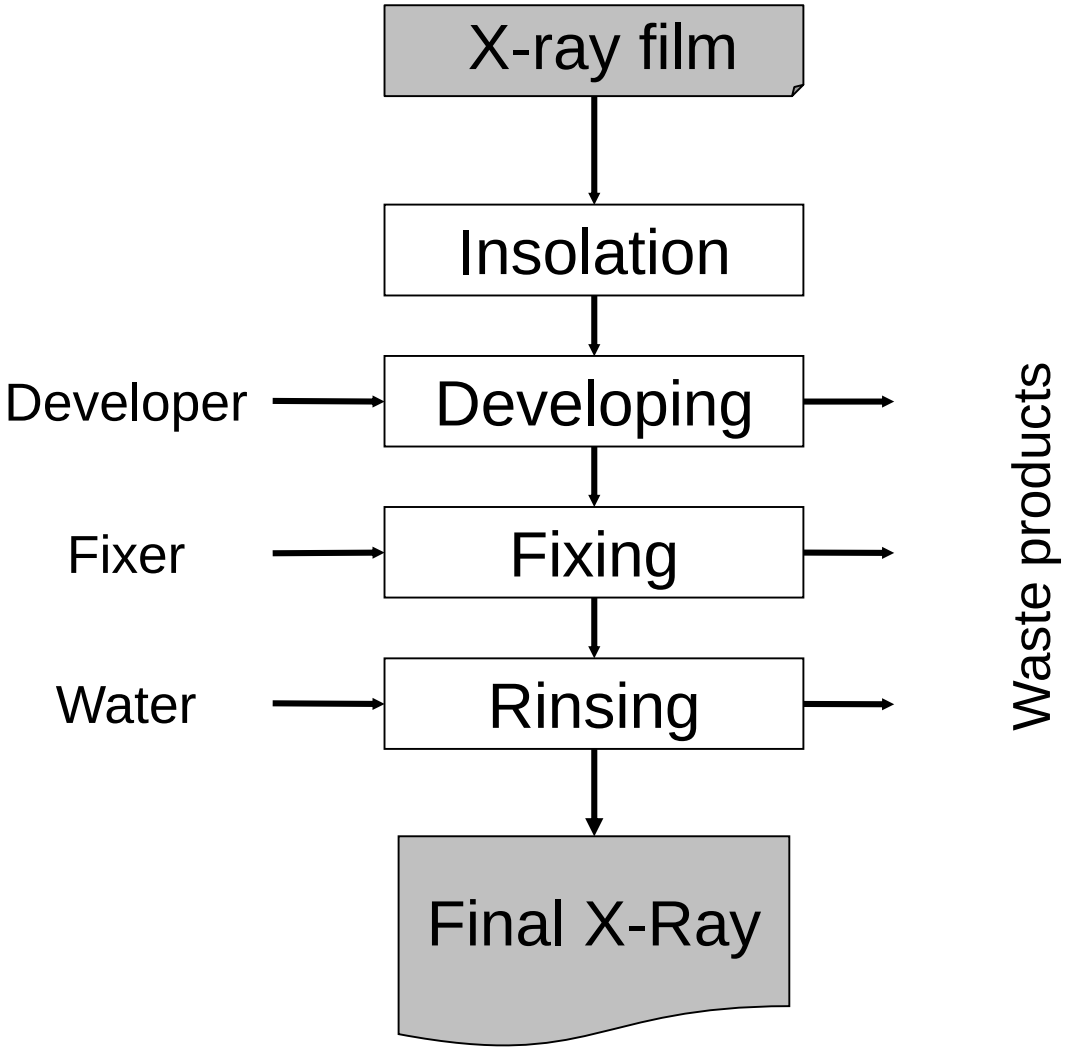


The shorter the wave length of the radiation
the higher the energy – the more dangerous!

Process Flow: Input - Output



The photographical processes



Background Information – Photo Chemicals

Some Facts:

- Average consumption per m² film:
  - about 500 ml usage of fixer.
- Ag is a component of X–ray films (Silver makes it possible to form an image)
- During processing the Ag removes from the film and goes into the fixer
- The used fixer has now an Ag concentration of about ~ 5 g/l
- The silver can on-line or off-line be recovered by electrolysis or with a metallic replacement cartridge

Background Information – Fixing Bath

- The pink container is developer and the greenish blue is the fixer.
- The container in back is the spent fixer, it goes to a recycler.
- In a typical x-ray processing operation, the fixer bath is continuously augmented with fresh fixer solution to maintain its quality and strength.
- Fixing Bathes are acidic and can cause skin irritations and allergic reaction
  - Ingredients: Ammonium thiosulfate

Background Information – Developing Bath

- In general, developing solution can be divided in the following types:
  - Acidic solutions with a pH < 2.0
  - Basic solutions with a pH > 12.5
  - Solutions containing formaldehyde
  - Solutions containing hydroquinone
  - Solutions containing potassium carbonate

Background Information – Rinse Water

- When developed images (films or papers) are moved from the fixer bath to the rinse, they still carry a small amount of silver, which is removed by the rinse water.
- Rinse waters contain low concentrations of silver ranging from less than 1 ppm to as high as 200 ppm.
- Although there is little economic benefit to recovering silver from rinse water, the environmental risk may prohibit discharge of untreated rinse water to treatment works or the environment if the silver concentration exceeds specified concentrations.

Background Information – X-ray Imaging Films

- X-ray imaging films often consist of polyethylene Terepthalate and a photosensitive material layer. The main constituent ingredients are:
  - Polyethylene Terepthalate 85 – 95 %
  - Gelatin 1 - 10 %
  - Polymers 1 – 10 %
  - Halogenated silver 0,05 – 1 %
  - Organic silver 1 – 10 %
  - Additives 0,1 – 11 %
- Discarded imaging films and papers are also silver-containing wastes. Since they are dry solid wastes, they are easily managed and are generally sold directly to a contractor for silver recovery.

Transport-Storage-Labelling

- Leakage proofed plastic container
- Sealable
- Label:

Environmental Impacts by Photochemicals

Examples – Please check the MSDS

Substance	Function	Environmental Impact
Hydroquinone	Developer	*Xn: Harmful;* *Water hazard class 1 (German Regulation): slightly hazardous for water*
Potassium carbonate	Developer	*Xn: Harmful;* *Water hazard class 1*
Ammonium Thiosulfate $(NH4)_2S_2O_3$	Fixing Solution	*Water hazard class 2: hazardous for water*

Environmental Impacts by Silver I

- Silver is released from image processing operations as silver thiosulfate, which degrades in the presence of oxygen to
  - primarily silver sulfide, and to a much lesser extent,
  - silver halide complexes.
- Unlike silver sulfides and halides, the hydrated or "free" silver ion is potentially toxic to aquatic organisms. However, this form of silver is rarely found in the environment because it combines so readily to form non-toxic complexes with common organic materials found in natural waters.

Environmental Impacts by Silver II

- The "free" form of silver is not a normal component of photographic and imaging waste streams.
- Although silver in its most common forms has no adverse human health effects and no apparent adverse environmental effects, because it is a precious metal capable of being reclaimed and reused, it is economically (and environmentally) sound to do so.
- Silver discharges can present problems for wastewater treatment plants with permit limitations for silver.

Internal Handling of Photo Chemicals

- Please ensure that:
  - MSDS for all chemicals are available
  - Spillage Procedures are trained
  - Occupational Safety Equipment is available
  - Developer and Fixer are not mixed!
  - Quality of the solutions is checked regularly
  - Container are labeled
  - Storage area is designated

Personal Protective Equipment

- **General protective and hygienic measures**
  - Keep away from foodstuffs, beverages and feed.
  - Immediately remove all soiled and contaminated clothing
  - Wash hands before breaks and at the end of work.
  - Avoid contact with the eyes.
  - Avoid contact with the eyes and skin.
- **Protection of hands:**
  - If skin contact cannot be avoided, protective gloves are recommended to avoid possible sensitization.
- **Eye protection:** Protective goggles are recommended.

Spill Response Procedure

- EQUIPMENT REQUIRED
  - Gloves • Bucket • Absorbent
  - Apron • Mop Materials
  - Goggles • Sponge
- SPILL RESPONSE PROCEDURES
  1. Put on gloves, goggles and an apron.
  2. Contain the spill with a mop or absorbent materials available.
  3. Check the appropriate material safety data sheet (MSDS) for special handling, ventilation, personal protection or other pertinent data.
  4. Clean up the spill, as directed, using generous amounts of water.
  5. Use the mop and sponge to clean the area thoroughly.
  6. Package and label all contaminated absorbent materials for off-site disposal.

Pollution Prevention Solutions I

- Pollution prevention and safer healthcare waste management options for X-ray processing solutions can be placed into one of three categories.

- This refers to the changes made to film processors to reduce the amount of waste solution produced through:

  - 1. Management practices
    - Process control
    - Inventory Control
    - Spill resource planning
    - Safety and Security of chemical storage areas and handling

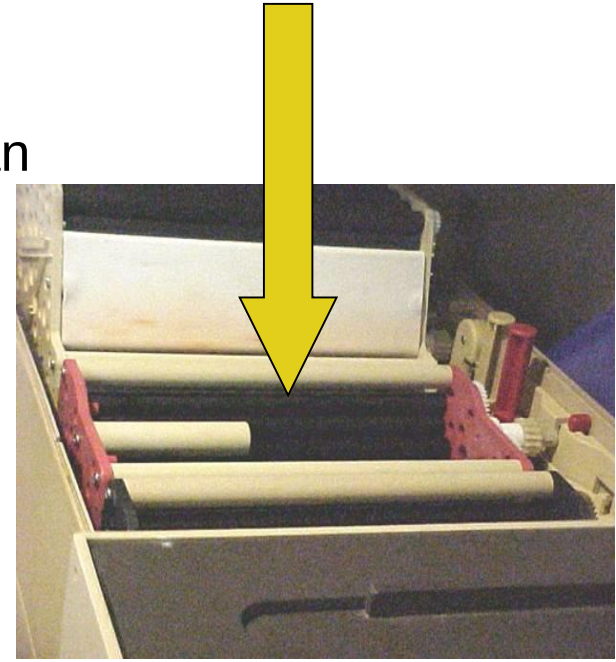
Pollution Prevention Solutions II

- 2. Equipment Modifications
  - Crossover/Squeegees
  - Stand by water saver
  - On-line silver recovery

- 3. Process Modifications
  - Solution regeneration and reuse
  - Water recycling and recovery
  - Dry chemicals and automated mixing

Squeezee / Water saver

- Crossovers/squeegees:
  - reduce carryover, therefore keeping the silver in the fixer tank where the overflow can be sent to silver recovery instead of being lost in the wash tanks.
  - are also used between the developer and fixer tanks. This minimizes developer carryover that can contaminate the fixer.
  - care and routine maintenance can extend the life and effectiveness of squeegees.
- Stand by Water saver
  - controls the wash water so it runs only when film is being processed.
  - When the film clears the machine, the wash goes into standby position and doesn't begin again until the next film is processed.

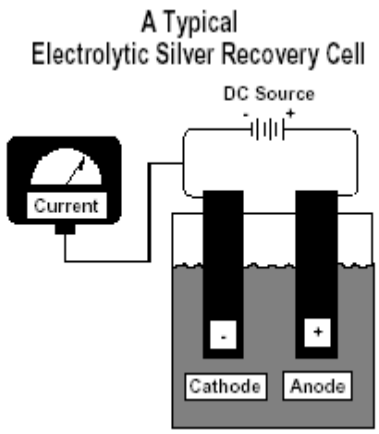


Reuse and Recycling potentials

- The silver of the fixing bathes can on-line or of-line be recovered by electrolysis or whit a metallic replacement cartridge
- By keeping the silver concentration in the fixer tank at a lower level, the amount of silver lost to the wash is significantly reduced.
- There are other benefits of in-line silver recovery. Generally, it's possible to use a lower fixer replenishment rate which means lower chemical consumption.
- Additionally, the silver recovered is high grade silver flake.

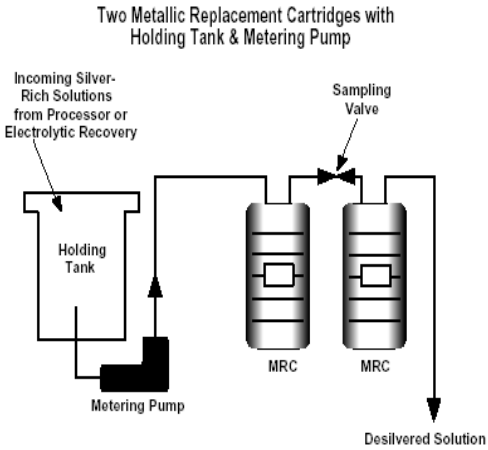
Silver recovery - electrolysis

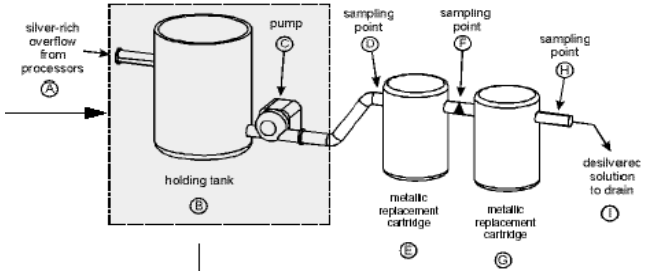
- Electrolytic silver recovery:
  - a direct current is passed through the solution between a positive electrode (the anode) and a negative electrode (the cathode).
  - Electron goes from cathode to the positively charged silver, converting it to its metallic state, which adheres to the cathode.
  - Simultaneous at the anode, an electron is taken from some species (Sulfite) in solution.
  - Cathode:
    - $Ag(S_2O_3)_2^{-3} + e^- \rightarrow Ag^0 + 2(S_2O_3)^{-2}$
  - Anode:
    - $SO_3^{-2} + H_2O \rightarrow SO_4^{-2} + 2H^+ + 2_{e-}$



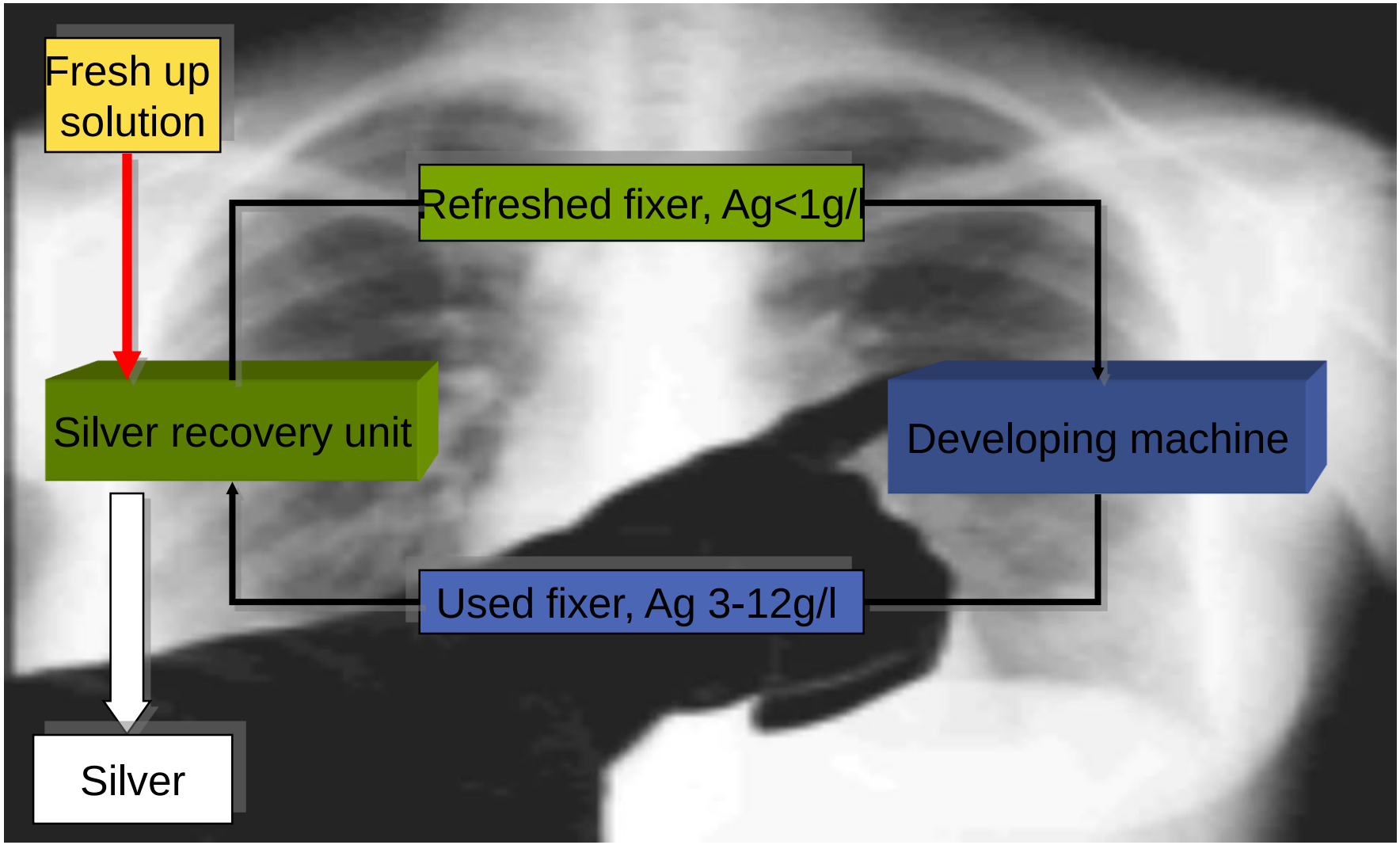
Silver recovery - Replacement

- Metallic replacement for silver recovery:
  - Process in which iron reacts with the silver thiosulfate in the solution to produce ferrous ions and metallic silver.
  - Commercial equipment: often referred to as Metallic Recovery Cartridges (MRCs)
  - Source of iron is fine steel wool (surface)
  - Replacement is a reduction-oxidation process:
    - $Ag(S_2O_3)_2^{-3} + Fe^0 \rightarrow 2Ag^0 + Fe^+ + 4S_2O_3^{-2}$
  - Silver concentration up to 5 mg/L.
  - Cheap and easy





On–line silver recovery



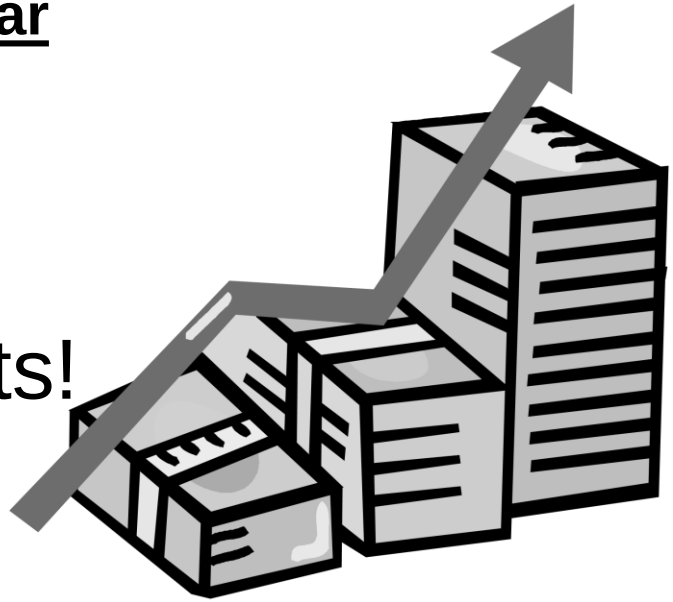
Overview: Benefits

- 90- 99 % silver recovery (of it about 90 % pure Ag)
- Income from silver selling
- Reduced cost for buying new fixer by ~ 50-70 %
- Reduction of chemical waste
- Reduce disposal costs

Financial example Silver Recovery:

- Example for a tertiary hospital:
  - Consumption: 500 litre/month (6 tons/year)
  - AG concentration = 5 g/l, recovery of 80%
  - 6 tons * 5 g/l * 80% = 24 kg/year Ag
  - 1 kg Ag = 510 US$ (per April 2015)
  - 24 kg * 510 US$/kg = **12,240 US$/year**

But:
Do not forget the necessary operation and investment costs!



Measuring silver concentration I

- Why measuring?
  - for process control,
  - for regulatory compliance
  - for waste characterization

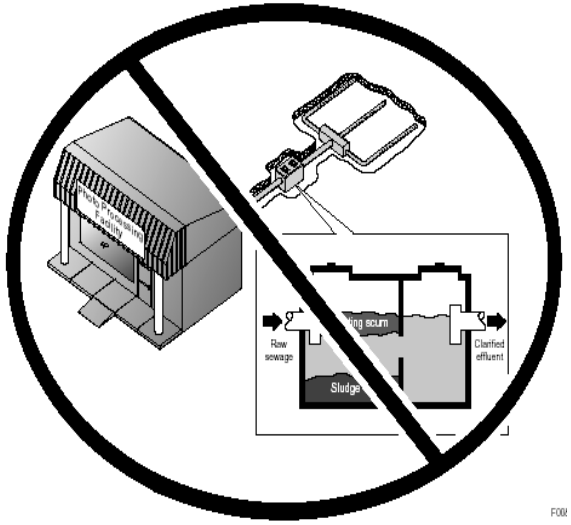
- Measurement techniques:
  - Qualitative Test Strips
    - Strip of paper that is impregnated with a silver-sensitive material.
    - The strip is dipped into the sample, discoloration indicates the presence of soluble silver.
    - To estimate silver concentrations greater than 1 gram/litre.

Measuring silver concentration II

- Measurement techniques II:
  - Colorimetry:
    - Adding a chemical to a sample that contains silver.
    - Silver reacts with the chemical to form a specific color. The color intensity is compared to a reference sample.
    - The difference in color corresponds to the concentration, it is able to detect silver as low as 30 ppm.
- Laboratory Test
  - For Total Recoverable Silver, Dissolved Silver, Leachable Silver
  - Methods:
    - Flame Atomic Absorption Spectroscopy (FAA)
    - Inductively Coupled Plasma Atomic Emission Spectroscopy

Disposal of Photo-Chemicals

- Normally best way: Specialized off-site treatment
  - Private Waste hauler
  - Hazardous household waste collection
- Indirect discharge
  - Treatment by the public waste water treatment plant
  - Treatment by on-site treatment plant
- Septic tank
  - Not recommended
  - Follow special procedure if no other possibility is given



Minimum Program – Photo-Chemicals

- In the case that no external disposal company is available, on-line silver recovery is not available and the waste treatment is carried out by septic tanks:
  1. Collect the developer and fixer separately.
  2. Take two 20 l containers and put about 10l steel wool in each.
  3. Pour the fixer in the first container and let it stand for a week.
  4. Check the silver concentration, if less than 1 g decant the fixer into the second container and let it stand for another week. Refill the steel wool if necessary.
  5. Check the silver concentration, if less than 0,5 g decant the fixer into an other container.
  6. Mix the de-silvered fixer with the developer.
  7. Pour the mixed photo chemicals very slowly into a sink, at the same time let water run to dilute the chemicals (1:3).
  8. If about 5 cm of sludge is visible in the containers, remove it out of the container and store it for sale.
- Follow safety instructions when handling photo chemicals (PPE, SOP, etc.)

External Treatment by Disposal Companies

Hospital:

- Developer
- Fixer
- Imaging Films

- External Treatment Plant
  - Electrolyte for Silver Recovery
  - Regeneration of solvents by distillation

Silver

Solvents

Waste:

- Incineration
- Landfill

Imaging Films without Silver

Central Photo Chemical Treatment

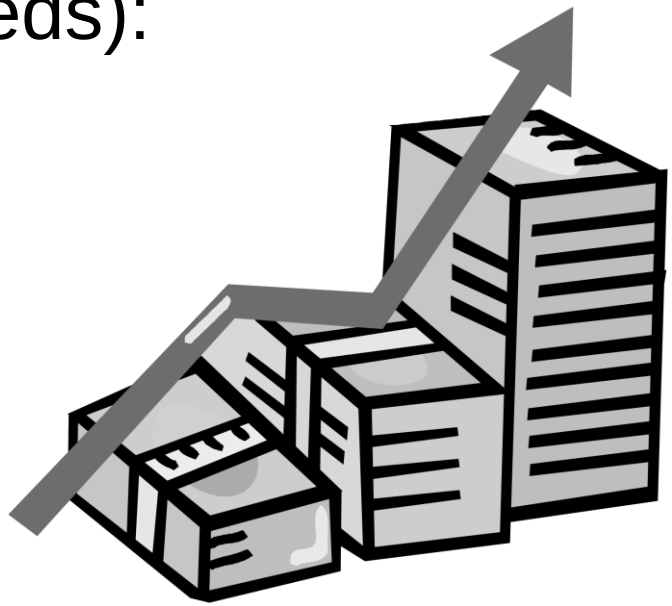
- Collection of the fixing bath for the treatment in a central treatment plant by a company
- Payment for the collection on kg basis
- Test of the silver concentration by test stripes
- Recovery of the silver in the central plant
- Payment for the recovery (kg)
- Reimbursement of the Silver

Duties of the External Treatment Unit

- Recover silver from all spent photochemicals such that the resulting level of silver does not exceed 5 mg/L after the terminal silver recovery unit;
- Have effluent concentrations that do not exceed the levels indicated below (Canadian Thresholds):
  - BOD_5: 300 mg/L,
  - Iron: 50 mg/L,
  - Sulphate: 1500 mg/L,
  - total phosphorus:10 mg/L;
  - pH 6 to 8
- Not require the use of chemical biocides/algacides;
- Provide the additional support of silver harvesting services to the user;
- Provide the additional support, optional to the user, of licensed pick-up of hazardous waste and other waste materials.

Financial example silver recovery:

- Example for a central 500 ton plant:
  - 500 tons * 5 g/l * 80% = 2,000 kg/year AG
  - 1 kg AG = 510 US$ (per April 2015)
  - 4000 kg * 510 US$/kg = **2,040,000 US$/year**
- Example for the client (300 beds):
  - Fixer generation: 2000 l p.y. – 5 g/l
  - AG generation: 10 kg = 5,100 US$
  - Cost for collection = 800 US$
  - Cost for recovery = 400 US$
  - Reimbursement = **3.900 US$**



SUMMARY

- Four main sorts of waste are generated: Fixing bath, developing bath, old X-ray films and rinsing water
- Not necessarily the silver is hazardous but the general chemicals in the photo chemicals
- Never pour developing bath down the drain
- Ensure that necessary management protocols are in place and the staff is provided with PPE
- Fixing bath can be reused by recovering the silver and fresh up of the solution
- If external services are used, a hand over protocol should be existent
- Fixing bath should be regularly tested – pH is not the appropriate indicator to measure the Ag content