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APPENDICES

APPENDIX A
ANALYTICAL EQUIPMENTS

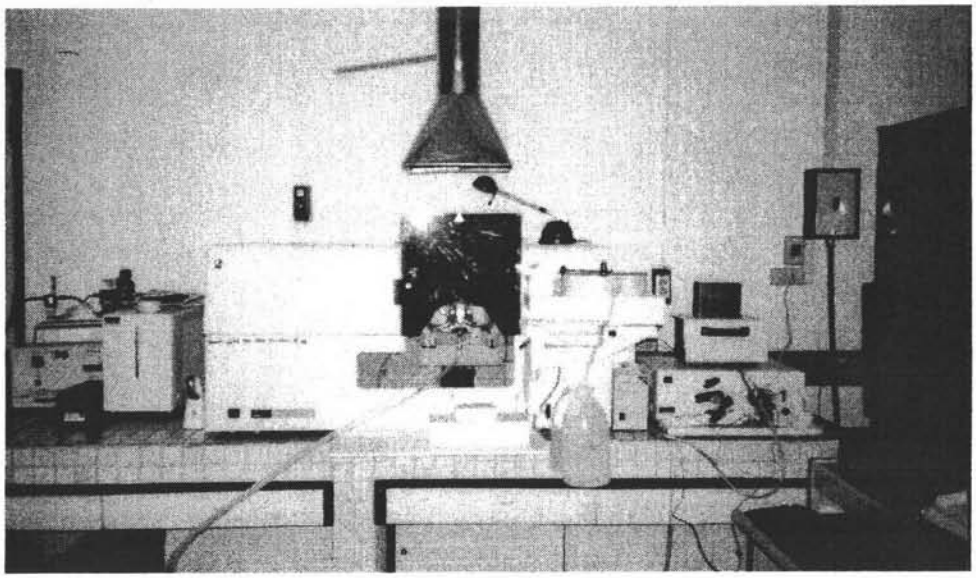

Figure A-1 Atomic Absorption Spectroscopy
(Perkin Elmer instrumemts Model AA analyst 800)

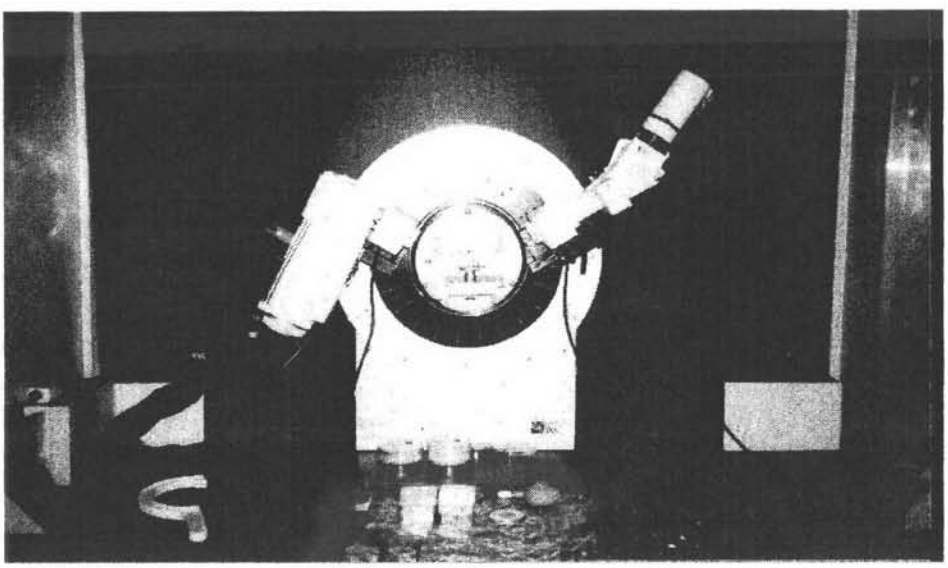

Figure A-2 X-Ray Diffractometer (Bruker Model D8 Advance)

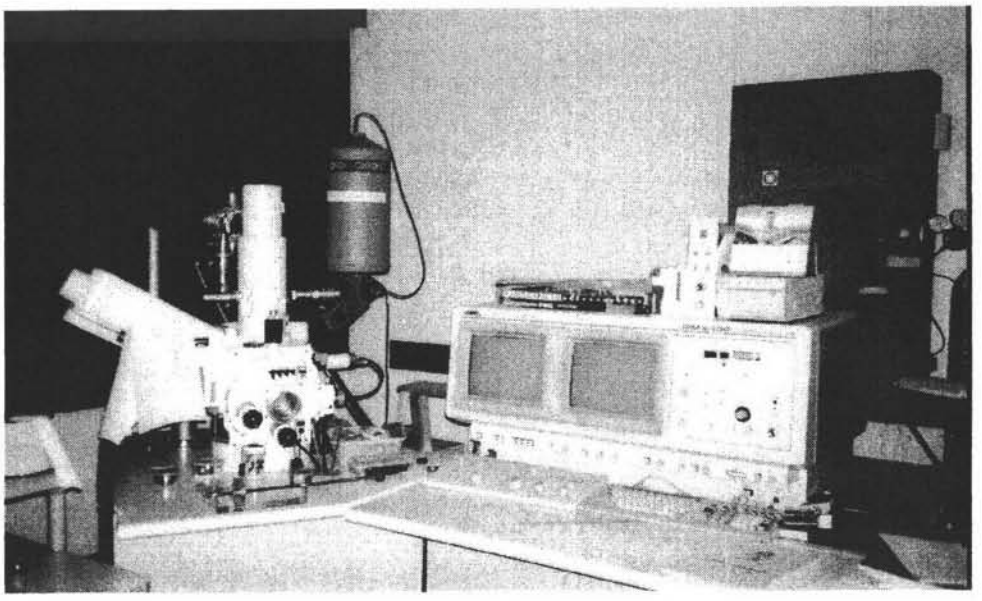

Figure A-3 Scanning Electron Microscope (JEOL Model JSM 6400) equipped with Energy Dispersive Spectroscopy

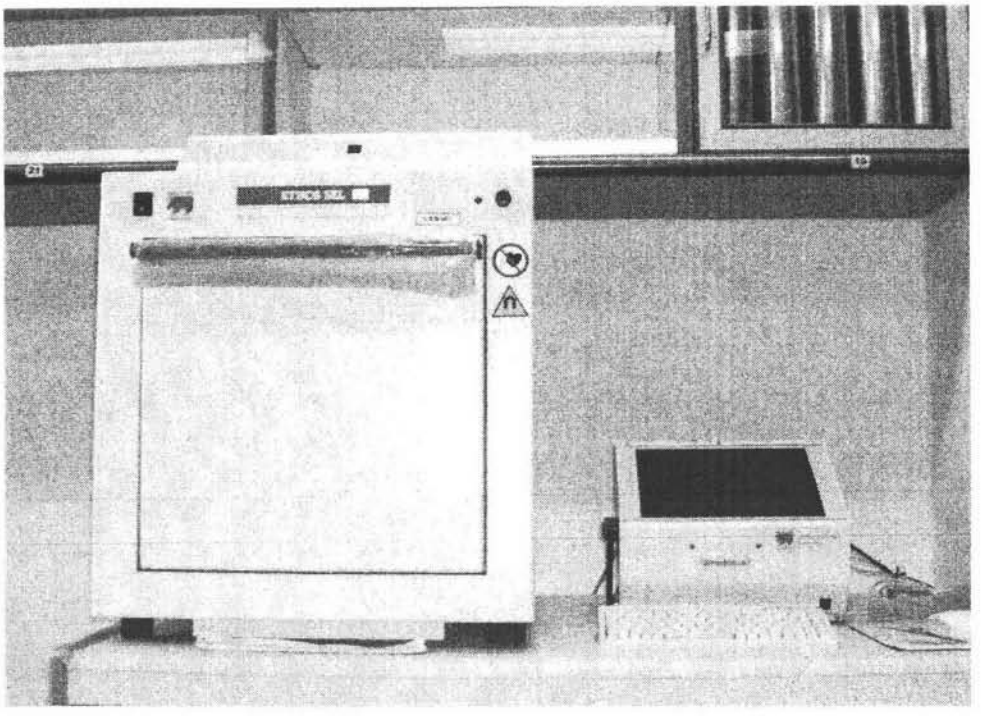

Figure A-4 Microwave for digestion (Milestone Model ETHOS SEI)

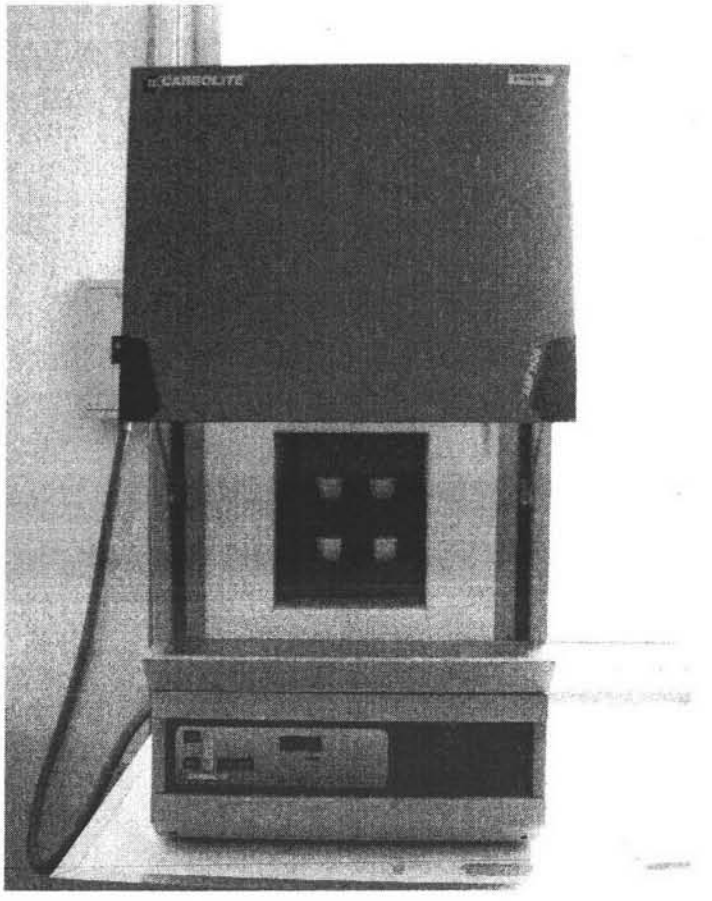

Figure A-5 Ashing Furnace (Cabolite Model AAF 1100)

APPENDIX B

CO_2 EMISSION CALCULATION

CO_2 EMISSION CALCULATION

B1. CO_2 Emission Factors

1) CO_2 emission factor of lignite

$$CO_2(kg/kW-hr) = 210.47 \frac{\text{lb}}{\text{mmBtu}} \times \frac{\text{kg}}{2.2046\,\text{lb}} \times \frac{\text{mmBtu}}{10^6\ \text{Btu}} \times \frac{10{,}107\text{Btu}}{\text{kW - hr}}$$

$$= 0.96\ \text{kg/kW - hr}$$

(Use primary kW-hr to Btu Number = 10,107 which is based on ca' 34% Efficiency)

2) CO_2 emission factor of natural gas

$$CO_2(kg/kW-hr) = 116.39 \frac{\text{lb}}{\text{mmBtu}} \times \frac{\text{kg}}{2.2046\,\text{lb}} \times \frac{\text{mmBtu}}{10^6\ \text{Btu}} \times \frac{10{,}107\text{Btu}}{\text{kW - hr}}$$

$$= 0.53\ \text{kg/kW - hr}$$

3) CO_2 emission factor of fuel oil

$$CO_2(kg/kW-hr) = 159.66 \frac{\text{lb}}{\text{mmBtu}} \times \frac{\text{kg}}{2.2046\,\text{lb}} \times \frac{\text{mmBtu}}{10^6\ \text{Btu}} \times \frac{10{,}107\text{Btu}}{\text{kW - hr}}$$

$$= 0.73\ \text{kg/kW - hr}$$

B2. Fuel used in Electricity Plant in Thailand.

For the calculation, natural gas was considered as a sole fuel, as it represented 68% of the fuel sources used for generating electricity Thailand (**Table B-1**).

Table B-1 Fuels used in Electricity Plant in Thailand in 2005.

Fuel source	%
Natural gas	68
Coal (Lignite)	15
Fuel oil	8
Hydro energy	5
Import and others	4

Source: Office of Energy Policy and Planning, Ministry of Energy, 2006

B3. CO_2 Emission from Leaching Process

Condition 1

Temperature: 100°C

Time: 20 min

Used film = 5 g in 50 mL of 5% oxalic acid solution

Equipment

1. Heater

1.1 Thermal energy required to heat up solution from 25°C to 100°C in 7 minutes

From $Q = mC_p\Delta T$ [joule]

m = Mass [g]

C_p = Specific Heat Capacity [J/g-°C]

T = Temperature [°C]

Substitute for: m = 55g,

C_p = 4.186 J/g°C,

ΔT = 100-25 =75 °C

So Q = (55)(4.186)(75)

= 17.27 kJ

1.2 Electrical heater used in the heat-up 7-minute period

= 140 W x 7 min x 60 s/min

= 58.80 kJ

1.3 Energy to compensate heat loss during 20 min retention time to maintain temperature at 100°C (Temp. control turned on ca. 10 minutes out of 20 minutes).

= 140 W x 10 min x 60 s/min

= 84 kJ

Total electrical energy used for leaching of 5 g used film @ 98%leaching efficiency = 58.80 + 84 = 142.8 kJ

$$= \frac{142.8\,\text{kJ}}{5\,\text{g}} \times \frac{1{,}000{,}000g}{ton}$$

$$= \frac{28{,}560{,}000kJ}{ton} x \frac{hr}{3600s}$$

$$= 7{,}933\ \text{kW-hr}$$

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 4,204.49 kg

2. Stirring

Power to mix 1 ton of used film in 2.5 m^3 acid solution is estimated to 5 Hp

$$= 5\,\text{Hp} \times 0.7457 \frac{[\text{kW}]}{[\text{Hp}]} \times \frac{20\,\text{min}}{60\,\text{min}}$$

$$= 1.24\text{kW - hr}$$

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 0.66 kg

3. Cooling

Power to supply a cooling unit is estimated to 20 Hp

$$= 20\,\text{Hp} \times 0.7457 \frac{[\text{kW}]}{[\text{Hp}]} \times \frac{20\,\text{min}}{60\,\text{min}}$$

$$= 4.97\text{kW - hr}$$

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 2.63 kg

4. Wastewater treatment

4.1 Assumption: leaching 1,000 kg of used film in 2.5 m^3 in acid solution

4.2 Amount of oxalic acid used = 125 kg in one batch

= 12.5 kg when reuse 10 times

$$1\,\text{kg oxalic acid} = \frac{32\,\text{kg COD}}{184} = 0.174\text{kg COD}$$

12.5 kg oxalic acid=0.174 kg COD x 12.5 = 2.175 kg COD

4.3 Amount of leached gelatin = 20% by weight of used film = 200 kg

$$1\,\text{kg gelatin} = \frac{6{,}208\,\text{kg COD}}{4{,}866} = 1.276\text{kg COD}$$

200 kg gelatin = 1.276 kg COD x 200 = 255.2 kg COD

4.4 Total COD = 2.175 + 255.2 = 257.375 kg COD

4.5 Energy for aeration in biological treatment = 1.5-2.5 kg O_2/kW-hr

Use average = 2 kg O_2/kW-hr

4.6 kW - hr needed for wastewater treatment $= \frac{257.375}{2} = 128.787$

4.7 CO_2 emission

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 68.26 kg

5. Total amount of CO_2 emission = 4,204.49 + 0.66 + 2.63 + 68.26

= 4,276 kg

Condition 2

Temperature: 90°C

Time: 60 min

Used film = 5 g in 50 mL of 5% oxalic acid solution

Equipment

1. Heater

1.1 Thermal energy required to heat up solution from 25°C to 90°C in 5 minutes

From $Q = mC_p\Delta T$ [joule]

m = Mass [g]

C_p = Specific Heat Capacity [J/g-°C]

T = Temperature [°C]

Substitute for: m = 55g,

C_p = 4.186 J/g°C,

ΔT = 90-25 =65 °C

So $Q = (55)(4.186)(65)$

$= 15$ kJ

1.2 Electrical heater used in the heat-up 5-minute period

= 140 W x 5 min x 60 s/min

= 42 kJ

1.3 Energy to compensate heat loss during 60 min retention time to maintain temperature at 90°C (Temp. control turned on ca. 10 minutes out of 60 minutes).

= 140 W x 10 min x 60 s/min

= 84 kJ

Total electrical energy used for leaching of 5 g used film @ 98%leaching efficiency = 42 + 84 = 126 kJ

$$= \frac{126\,\text{kJ}}{5\,\text{g}} \times \frac{1{,}000{,}000g}{ton}$$

$$= \frac{25{,}200{,}000kJ}{ton} x \frac{hr}{3600s}$$

= 7,000 kW-hr

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 3,710 kg

2. Stirring

Power to mix 1 ton of used film in 2.5 m^3 acid solution is estimated to 5 Hp

$$\text{unit} = 5\,\text{Hp} \times 0.7457 \frac{[\text{kW}]}{[\text{Hp}]} \times 1hr$$

$$= 3.73\text{kW - hr}$$

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 1.98 kg

3. Wastewater treatment

3.1 Assumption leaching 1,000 kg of used film in 2.5 m^3 in acid solution

3.2 Amount of oxalic acid used = 125 kg in one batch

= 12.5 kg when reuse 10 times

1 kg oxalic acid=32/184 kg COD = 0.174 kg COD

12.5 kg oxalic acid=0.174 kg COD x 12.5 = 2.175 kg COD

3.3 Amount of leached gelatin = 20% by weight of used film = 200 kg

1 kg gelatin = 6,208/4,866 kg COD = 1.276 kg COD

200 kg gelatin = 1.276 kg COD x 200 = 255.2 kg COD

3.4 Total COD = 2.175 + 255.2 = 257.375 kg COD

3.5 Energy for aeration in biological treatment = 1.5-2.5 kg O_2/kW-hr

Use average = 2 kg O_2/kW-hr

3.6 kW-hr needed for wastewater treatment = 257.375/2 = 128.787

3.7 CO_2 emission

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 68.26 kg

4. Total amount of CO_2 emission = 3,710 + 1.98 + 68.26 = 3,780 kg

B4 CO_2 Emission from Existing Technology

Condition

Temperature: 1200°C

Time: 6.67 hr

Used film = 1,000 kg

Equipment

1. Furnace

1.1 Power of blower = 253.5 Hp

$$\text{unit} = 253.5\ \text{Hp} \times 0.7457 \frac{[\text{kW}]}{[\text{Hp}]} \times 6.67 hr$$

$$= 1{,}260.863 \text{kW - hr}$$

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 668.26 kg

1.2 Fuel oil

$$\text{Fuel oil} = 80 \frac{[\text{l}]}{[\text{hr}]}$$

$$\text{Fuel oil} = 80 \frac{[\text{l}]}{[\text{hr}]} \times 6.67[hr] = 533.6l$$

$$\text{unit} = 533.6\,[\text{l}] \times \frac{0.985\,[\text{kg}]}{[\text{l}]} \times \frac{10^7 [cal]}{[kg]} \times \frac{4.186[W-s]}{[cal]} \times \frac{1[hr]}{3600[s]}$$

$$= 6{,}111.513 \text{kW - hr}$$

CO_2 emission factor of fuel oil = 0.73 kg/kW-hr

The amount of CO_2 emission = 4,461.40 kg

2. Cooling

Power of an equipment = 8 Hp

$$\text{unit} = 8\ \text{Hp} \times 0.7457 \frac{[\text{kW}]}{[\text{Hp}]} \times 6.67 hr$$

$$= 39.791 \text{kW - hr}$$

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 21.08 kg

3. Bag filter

Power of an equipment = 61.9 Hp

$$\text{unit} = 61.9\ \text{Hp} \times 0.7457 \frac{[\text{kW}]}{[\text{Hp}]} \times 6.67 hr$$

$$= 307.879\ \text{kw - hr}$$

CO_2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 163.18 kg

4. Scrubber

Power of an equipment = 21.8 Hp

$$\text{unit} = 21.8\ \text{Hp} \times 0.7457 \frac{[\text{kW}]}{[\text{Hp}]} \times 6.67 hr$$

$$= 108.429\ \text{kW - hr}$$

CO2 emission factor of natural gas = 0.53 kg/kW-hr

The amount of CO_2 emission = 57.47 kg

5. Total amount of CO_2 emission = 668.26 + 4,461.40 + 21.08 + 163.18 + 57.47

= 5,371.39 kg

APPENDIX C
QUESTIONNAIRS

Radiographic Films Importer Questionnaire

Organization/Name _____

Address _____ Moo _____ Soi _____ Road _____

Tambol _____ Amphur/District _____ Province _____

Postal code _____ Tel. _____

---

1. The objectives of radiographic films importing

Objective	Proportion (%)
☐ For sell	
☐ Industrial use	
Total	

2. Amount of radiographic film selling in Thailand (average during last year)

Types of buyer	Selling amount (%)
☐ Hospital	
☐ Factory	
☐ Others (Please describe) _____	
Total	

Name (Signature)_____

Block Letter

(_____)

Position _____

Date _____

Radiographic Films, Developer and Fixer Using Questionnaire

No. _____

Hospital's name _____ amount of beds _____

Address _____ Moo _____ Soi _____ Road _____

Tambol _____ Amphur/District _____ Province _____

Postal Code _____ Tel. _____

Name _____ Position _____

Using and Management Information of Radiographic Films, Developer and Fixer

1. Radiographic Films

1.1 Radiographic films consumption

	2002	2003
1) Amount of consumption per year (Boxes)		
2) Film expense per year (Baht)		
3) Name of suppliers	3.1 _____ 3.2 _____ 3.3 _____	3.1 _____ 3.2 _____ 3.3 _____

1.2 Radiographic films consumtion according to their size

Size	Number of sheet per boxes	Net weight (gram/box)	Using amount/year (boxes)		Remark
			2002	2003	
☐ 8 inc. X 7 inc.					
☐ 8 inc. X 10 inc.					
☐ 10 inc. X 12 inc.					
☐ 12 inc. X 15 inc.					
☐ 14 inc. X 17 inc.					
☐ _____					
☐ _____					
☐ _____					
Total					

1.3 Film processing

- ☐ Automatic processing
- ☐ Manual processing

1.4 Used Radiographic films management (after collected for _____ years)

- ☐ Send to the supplier
- ☐ Burn in hospital's incinerator
- ☐ Burn in other organization's incinerator
- ☐ Sell (please fill in 1.5)
- ☐ others (please describe) _____

1.5 Used radiographic films selling

	2002	2003
1) Amount of selling per year (Tons)		
2) Income from selling (Baht)		
3) Buyer's name	Name _____ Address _____ _____ Tel. _____	Name _____ Address _____ _____ Tel. _____

2. Developer

2.1 Developer consumption

	2002	2003
1) Amount of consumption per year (Litre, gallon*)		
2) Developer cost per year (Baht)		
3) Name of suppliers	3.1 _____ 3.2 _____ 3.3 _____	3.1 _____ 3.2 _____ 3.3 _____

Remark : * in case of gallon, please inform "1 gallon = _____ litre"

2.2 Spent Developer Management

- ☐ Send to the supplier
- ☐ Send to hospital wastewater treatment plant
- ☐ Send to domestic wastewater treatment plant
- ☐ sell (please fill in 2.3)
- ☐ Others (please describe)_____

2.3 Spent Developer Selling

	2002	**2003**
1) Amount of selling per year (Litre, gallon*)		
2) Income from selling (Baht)		
3) Buyer's name	Name _____ Address _____ _____ Tel. _____	Name _____ Address _____ _____ Tel. _____

Remark: * in case of gallon, please inform "1 gallon = _____ litre"

3 Fixer

3.1 Fixer consumption

	2002	**2003**
1) Amount of consumption per year (Litre, gallon*)		
2) Fixer cost per year (Baht)		
3) Name of suppliers	3.1 _____ 3.2 _____ 3.3 _____	3.1 _____ 3.2 _____ 3.3 _____

Remark: * in case of gallon, please inform "1 gallon = _____ litre"

3.2 Spent Fixer Management

- ☐ Send to the supplier
- ☐ Send to hospital wastewater treatment plant
- ☐ Send to domestic wastewater treatment plant
- ☐ Sell (please fill in 3.3)
- ☐ Others (please describe) _____

3.3 Spent Fixer Selling

	2002	**2003**
1) Amount of selling per year (Litre, gallon*)		
2) Income from selling (Baht)		
3) Buyer's name	Name _____ Address _____ _____ Tel. _____	Name _____ Address _____ _____ Tel. _____

Remark: * in case of gallon, please inform "1 gallon = _____ litre"

How to select the buyer/waste dealer of used films and spent fixer

1) Kind of waste dealer (you can answer more than 1 item)

- ☐ General person
- ☐ Juristic person
- ☐ Both of general and juristic person

2) Documentation (you can answer more than 1 item)

- ☐ Copy of national identification card
- ☐ Copy of business establishment license
- ☐ Copy of resident registration certificate
- ☐ Copy of factory-operation permit
- ☐ Others (please describe) _____

3) Criteria of selection (you can answer more than 1 item)

- ☐ Price
- ☐ Waste treatment permit
- ☐ Others (please describe) _____

Date _____

APPENDIX D

UNIFORM OF HAZARDOUS WASTE MANIFEST

หมายเลขใบกำกับการขนส่งของเสียอันตราย : Manifest No.

ใบกำกับการขนส่งของเสียอันตราย

(Uniform Hazardous Waste Manifest)

1. ส่วนของผู้ก่อกำเนิดของเสียอันตราย: This section must be completed by the Generator

1) ชื่อ : name .....
สถานก่อกำเนิด : Generator address .....

2) เลขประจำตัวผู้ก่อกำเนิดของเสียอันตราย : Generator's ID .....
โทรศัพท์ : Phone ..... โทรสาร : Fax .....กรณีฉุกเฉิน : Emergency .....

3) ผู้ขนส่งของเสียอันตราย : Transporter

รายที่ 1 ชื่อบริษัท : First company name .....
เลขประจำตัวผู้ขนส่งของเสียอันตราย รายที่ 1 : Transporter's ID .....

รายที่ 2 ชื่อบริษัท : Second company name .....
เลขประจำตัวผู้ขนส่งของเสียอันตราย รายที่ 2 : Transporter's ID .....

4) ผู้ที่รวบรวม บำบัด และกำจัดของเสียอันตราย : Treatment Storage Disposal Facilities (TSDFs)

รายที่ 1 ชื่อบริษัท : First TSDF's name .....
เลขประจำตัวผู้เก็บรวบรวม บำบัด และกำจัดของเสียอันตราย รายที่ 1 Disposer's ID .....

รายที่ 2 ชื่อบริษัท : Second TSDF's name .....
เลขประจำตัวผู้เก็บรวบรวม บำบัด และกำจัดของเสียอันตราย รายที่ 2 Disposer's ID .....

5) รายละเอียดของของเสียอันตรายที่ขนส่งคลื่อนย้าย :

ลำดับ No.	รายละเอียด (Description)	รหัสของเสียอันตราย : Waste ID.	หมวดข้อวัสดุที่ไม่ใช้แล้ว หมวด	ข้อ	ภาชนะบรรจุ : Containers จำนวน : No.	ชนิด : Type	ปริมาตรสุทธิ : Quantity	หน่วยน้ำหนัก : Unit Wt / Vol	รายละเอียดเพิ่มเติม : Additional Information

รวมปริมาตรของเสียอันตรายทั้งหมด : Total Quantity ของเหลว : liquid ..... ลิตร/ลูกบาศก์เมตร : Liters/cu.m ของแข็ง : solid .....กิโลกรัม / ตัน : Kgs. / tons

6) การปฏิบัติที่มีลักษณะพิเศษ และข้อมูลเพิ่มเติม
Special handling Instructions and additional information

7) คำรับรอง : ข้าพเจ้าขอรับรองว่าได้ส่งมอบของเสียอันตรายแล้วตามที่ระบุข้างต้น และมีการบรรจุผลิตป้ายหรือฉลากอย่างเหมาะสมครบถ้วนตามข้อกำหนดของกฎหมายทุกประการ :
Generator Certificate : I hereby declare that the contents of this consignment are accurately described above and have been packed and labeled and are in proper condition for transport according to regulation
ลงชื่อ Generator's name ..... ลายเซ็น : Signature ..... วันที่ : Date ..... เดือน : Month ..... พ.ศ : Year .....

2. ส่วนของผู้ขนส่งของเสียอันตราย: This section must be completed by the Transporter

1) ชื่อผู้ขนส่งรายที่ 1 : Transporter's name .....
เลขประจำตัวผู้ขนส่ง : Transporter's ID .....
โทรศัพท์ : Phone ..... โทรสาร : Fax .....ฉุกเฉิน : Emergency .....

2) พาหนะที่ใช้ Vehicle	รถบรรทุก Truck	รถไฟ Train	เรือ Ship	เครื่องบิน Plane
3) เลขทะเบียนพาหนะ : Vehicle ID				

4) คำรับรอง : ข้าพเจ้าขอรับรองว่าได้รับของเสียอันตรายแล้วตามที่ระบุข้างต้น และการขนส่งเป็นไปตามข้อกำหนดของกฎหมายทุกประการ
Transporter Certification : I hereby declare that I have received the type and quantity of waste as described above by the generator and that waste has been transported according to regulations.
โดยขนส่งจากจังหวัด : From .....ไปยังจังหวัด To..... ใช้ระยะเวลาประมาณ : Time spending .....ชม./วัน : hours/day
ลงชื่อผู้ขนส่งรายที่ 1 Transporter's name ..... ลายเซ็น : signature ..... วันที่ : Date.....เดือน : Month..... พ.ศ Year.....

5) ชื่อผู้ขนส่งรายที่ 2 : Transporter's name.....
เลขประจำตัวผู้ขนส่ง : Transporter's ID .....
โทรศัพท์ : Phone ..... โทรสาร : Fax ..... ฉุกเฉิน : Emergency .....

6) พาหนะที่ใช้ Vehicle	☐ รถบรรทุก Truck	☐ รถไฟ Train	☐ เรือ Ship	☐ เครื่องบิน Plane
7) เลขทะเบียนพาหนะ : Vehicle ID				

8) คำรับรอง : ข้าพเจ้าขอรับรองว่าได้รับของเสียอันตรายแล้วตามที่ระบุข้างต้น และการขนส่งเป็นไปตามข้อกำหนดของกฎหมายทุกประการ
Transporter Certification : I hereby declare that I have received the type and quantity of waste as described above by the generator and that waste has been transported according to regulations.
โดยขนส่งจากจังหวัด : From .....ไปยังจังหวัด To..... ใช้ระยะเวลาประมาณ : Time spending .....ชม./วัน : hours/day
ลงชื่อผู้ขนส่งรายที่ 2 Transporter's name ..... ลายเซ็น : signature ..... วันที่ : Date.....เดือน : Month..... พ.ศ : Year.....

3. ส่วนของผู้ประกอบการสถานเก็บรวบรวม บำบัด และกำจัดของเสียอันตราย: This section must be completed byTSDFs

1) ชื่อผู้รับกำจัด TSDF's name .....
สถานที่กำจัด : TSDF's address .....

2) เลขประจำตัวผู้รับกำจัด :TSDF's ID.....
โทรศัพท์ : Phone .....โทรสาร : Fax .....กรณีฉุกเฉิน : Emergency.....

3) คำรับรอง ข้าพเจ้าขอรับรองว่าได้รับของเสียอันตรายแล้วตามปริมาณที่ระบุข้างต้นนี้
TSDF certificate of arrival : I hereby declare that I have received the reference load.
และสามารถกำจัดของเสียที่รับมานี้ได้ภายในระยะเวลา Treatment period..... ☐ วัน : day ☐ เดือน :month ☐ ปี : year นับจากวันที่ได้รับของเสีย : since the day that received waste
ลงชื่อผู้รับกำจัด : TSDF 's name ..... ลายเซ็น : Signature .....วันที่ : Date.....เดือน : Month..... พ.ศ. : Year.....

4) กรณีของเสียอันตรายไม่ตรงตามที่แจ้ง : Discrepancy Notification
ประเภทของเสียอันตราย : Type of waste..... ปริมาณ: Quantity.....
การดำเนินงาน : Action taken ส่งคืน : Returned จัดประเภทใหม่ : Reclassified / รหัส : Waste ID..... ☐ รับกำจัด : Accepted เหตุผล : Reason of action .....
วันที่ส่งคืน : Date returned ...../...../.....(วัน/เดือน/ปี :dd / mm / yy) หมายเลขใบกำกับการขนส่งของเสียอันตรายที่ส่งกลับ : Returned manifest no .....
ชื่อผู้ส่งคืน TSDF 's name ..... ลายเซ็นผู้ส่งคืน : TSDF's Signature.....

APPENDIX E
PUBLISHED PAPERS

Clean Techn Environ Policy
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ORIGINAL PAPER

Policy concept applied to X-ray waste management in Thailand

P. Khunprasert · N. Grisdanurak · J. Thaveesri · V. Danutra · W. Puttitavorn

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Abstract In Thailand, 98.5% of the imported X-ray films are used for medical services. After the developing process, approximately 55–65% of metallic silver still remains on the developed X-ray films. The used films are practically kept at the hospitals for record-keeping purposes for 5–10 years, while the developing agents are reused at minimal twice. The discarded films and the spent (fixer) solution are normally sold to waste dealers prior to their delivery to waste processors for silver recovery. To recover silver, typically, the used films are chemically leached; the spent solution is processed by electrolysis technique. Nevertheless, the recovery processes also generate toxic chemical wastes, which are commonly spilled or discharged into the environment without any proper treatment and disposal. The dealers for X-ray waste are one of the major stakeholders who are apparently exempted from state control and regulations; but, depending on its size and capacity, the processors must have a factory-operating permit. It appeared that the key regulators of X-ray waste are the Ministry of Industry and the Ministry of Public Health. In this study, the monitoring and tracking of silver-contaminated wastes were strictly carried out from the generation points to their ultimate disposals. A fact sheet of the management of X-ray waste has been proposed.

Keywords X-ray waste · Waste management · Fact sheet

Abbreviations

Ag^0	Metallic silver
Ag^+	Silver ion
AgX	Silver halide
F	Material flow into and out for each hospital inside the control volume
F&M	Fabrication and manufacturing
HA	Hospital accreditation
MOI	Ministry of Industry
MOPH	Ministry of Public Health
PWG	Primary waste generator
S	The stock of material retained or depleted from the reservoir over a time period
SWG	Secondary waste generator
WD	Waste dealer
WG	Waste generator
WP	Waste processor
WR	Waste regulator

P. Khunprasert · V. Danutra
National Research Center for Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok 10330, Thailand

N. Grisdanurak (✉)
Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Klong-Luang, Pathumtani 12120, Thailand
e-mail: gnurak@engr.tu.ac.th

J. Thaveesri
Department of Industrial Works, Ministry of Industry, Bangkok 10400, Thailand

W. Puttitavorn
Environmental Research Institute, Chulalongkorn University, Bangkok 10330, Thailand

Introduction

Silver is a precious metal, which can be feasibly recycled from its contaminated wastes. With an increasing demand for silver in the world, the secondary production of silver from scraps and other forms of wastes has become a new supply in the market (Handerson 2003). Owing to its considerable silver content, X-ray waste (i.e., used films and spent fixer) is one of secondary silver sources, which has recently been focused on.

To date, there have been few articles reported on the cycles of silver (Johnson et al. 2005; Lanzano et al. 2006). These articles have described the stock and flow of the silver cycle in an overall depiction focused on the industrial usage of silver from its ore extraction to its final disposal. Therefore, an investigation on the flow patterns of silver originated from X-ray waste was undertaken in this study in order to improve its management system in Thailand.

X-ray films contain greater amounts of silver than that in any other types of film due to the radiation-sensitive silver halide (AgX), which is scattered on the gelatin of the emulsion layer on both sides of a polyester sheet (i.e., the film base). Traditionally, 94–98% of X-ray films are used in medical services, e.g., chest X-rays, mammograms, CT scans, etc. Annually, X-ray films of ca. 2 billions are commercialized around the world (Gambhir 2004).

In the developing process of X-ray films, light-exposed silver ions (Ag^+) are reduced by a developer solution to metallic silver (Ag^0) and retained on the film. The unexposed silver is then dissolved in the form of silver thiosulfate into the fixer solution (Colorado Industrial Pretreatment Coordinators Association 2004). The overall development process of an X-ray film is illustrated Fig. 1. Wastes such as film scraps, spent fixer, spent developer, rinse-water, and spilled chemicals are mainly generated within hospital radiology departments' premise.

With respect to recovery technologies, there are several techniques for recycling of silver from certain photographic wastes such as developed films and spent (developer or fixer) solution. There are four common methods being used to leach silver metal from used X-ray films, which are thermal (Hochberg 1989), biological (Fujiwara et al. 1991; Ishikawa et al. 1993), mechanical or physical (Hochberg 1989; Buser and Retting 1988), and chemical treatments (Moreno 1986; Messerschmidt 1988; Laungchonlatan 1988; Ajiwe and Anyadiegwu 2000; Syed et al. 2002). The first method relies on combustion for the recovery of silver and energy; while the rest not only recover silver, but also recycle the film base. The silver sludge, obtaining from the latter three methods, is smelted and further refined to form silver ingot.

Silver can be recovered from the spent fixer solution by electrolysis (Bourges et al. 2002), metallic replacement, chemical precipitation, reverse osmosis and ion exchange (Atia 2005; Cerjan-Stefanovic et al. 1991). The last two methods provide a way of increasing silver concentrations in a waste solution, so they are suitable for solutions with low silver content, i.e., rinse water and spent developer solution. Electrolysis and metallic replacement are effective methods that lead in a straightforward way to the retrieval of silver ingot. A simple depiction of these recovery methods is shown in Fig. 2. Recently, some researchers have confirmed the

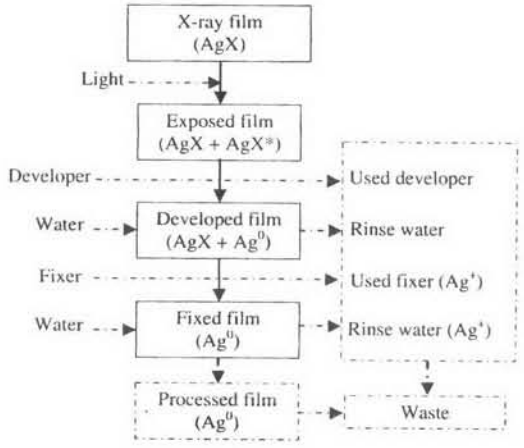

Fig. 1 Development process of X-ray films

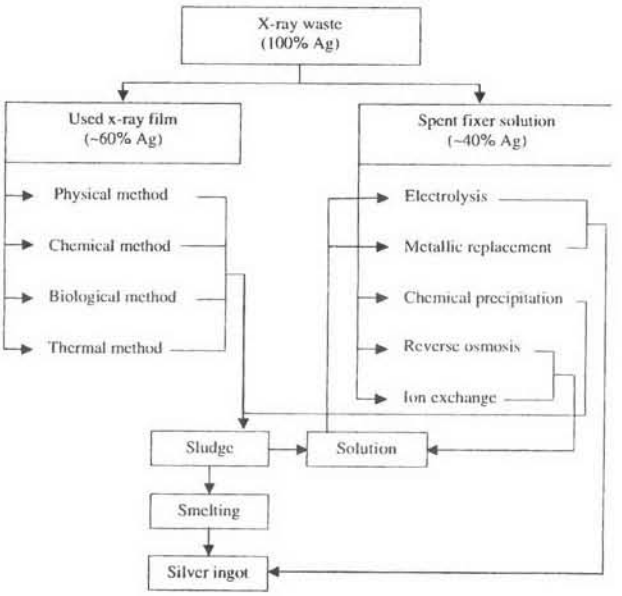

Fig. 2 Techniques for the recovery silver from X-ray waste

effectiveness of a technique for the recovery of silver from spent fixer solution by the silver's adsorption to activated carbons (Adani et al. 2005) and to chitin (Songkroah et al. 2004).

X-ray waste poses potential hazards towards public health and the environment because it typically contains significant concentrations of silver. Silver, Ag^+ and its compounds have been reported to have higher bioconcentration factors in marine flora and fauna than in the fresh water organisms. Though it seems that the accumulation of silver by terrestrial plants from soils is low; silver (as silver nitrate) showed an adverse effect on sensitive laboratory mammals at total concentrations as low as 250 μg/l in drinking-water (brain histopathology), 6 mg/kg in diet (high accumulation in kidneys and liver), or 13.9 mg/kg body weight (lethality) (World Health Organization 2002). X-ray waste is generally considered hazardous when contaminated with silver to a certain extent. The United States Environmental Protection Agency (USEPA 2006) defines a solid waste containing silver in excess of 5 mg/l, determined by the Toxicity Characteristic Leaching Procedure (TCLP), as category D011 hazardous material.

Of importance, there is little information on how X-ray waste is manipulated in Thailand. Most researches (Tameerak 1979; Seelsaen 2001; Songkroah 2004) focused on technology for silver recovery from the waste more than on management policy. This paper reports on the present situation of X-ray waste in Thailand with emphasis on material flow analysis of silver and proposes future prospects for its management.

Present situation of X-ray waste management in Thailand

One important tool of industrial ecology based upon the law of conservation of mass to monitor the flow of specific substances is a Substance Flow Analysis (SFA). SFA is used for identifying environmental problems and proposing remedial/prevention strategies (Kapur 2006). In this study, the existing situation of X-ray waste management in Thailand is explained through a SFA to determine how much silver is disposed of into the environment. The flow of silver consists of four stages which are (1) production, (2) fabrication and manufacturing (F&M), (3) use, and (4) waste management (WM). In this analysis, the system boundary only limits the flow of silver in the production and F&M stages. A flow diagram of the silver waste life cycle is presented in Fig. 3.

A mass balance equation has been formulated to access the flow patterns of the silver waste cycle. It determines the recovered and lost amounts and establishes the amount entering the material reservoirs.

The mass balance equation is as follows:

$$dF/dt = \sum F_{\text{input}} - \sum F_{\text{output}} + \sum (S_t - S_{t-1}), \quad (1)$$

where F represents the material flow into and out for each hospital inside the control volume and S represents the stock of material retained or depleted from the reservoir over a time period.

Production of X-ray waste

In a production phase, it was found that there is currently no film manufacturer in Thailand and X-ray film products are all imported. Silver flows in an active form (AgX), coated on the X-ray film, into the study boundary. The application of the film has been mainly used for medical purposes. It was found that 98.5% of imported films are distributed to hospitals, medical institutes, and clinics; these utilizers produce wastes at their premise and become the primary waste generators (PWGs).

The stocks of silver did not change from year to year; this was due to the fact that a procurement amount of new X-ray films is carried out on an annual basis and the amount of used films, i.e., retained silver primarily depends upon the space of the used film collection area in each hospital. For example, for the year 2003–2004, the accumulation term approaches zero under steady-state conditions. The net accumulation of material equals to the summation of silver influx minus silver outflow in a defined control volume. Hence, Eq. 2 can be written as follows:

$$F_{\text{silver}} = \sum F_{\text{input}(2004)} - \sum F_{\text{output}(2004)} + \sum S_{(2004)} - \sum S_{(2003)}. \quad (2)$$

All X-ray films are imported by the suppliers, and their quantity is recorded by the Department of Customs, under the Ministry of Finance. Figure 4 indicates the amount of imported film from 2001–2005. The annual imported amount of film has increased in 2002 and then remains stable at a range of 630–640 ton. According to ca. 2% silver content (by weight) in X-ray film, this amounts to 12.7 ton of silver as the main material input in the defined system.

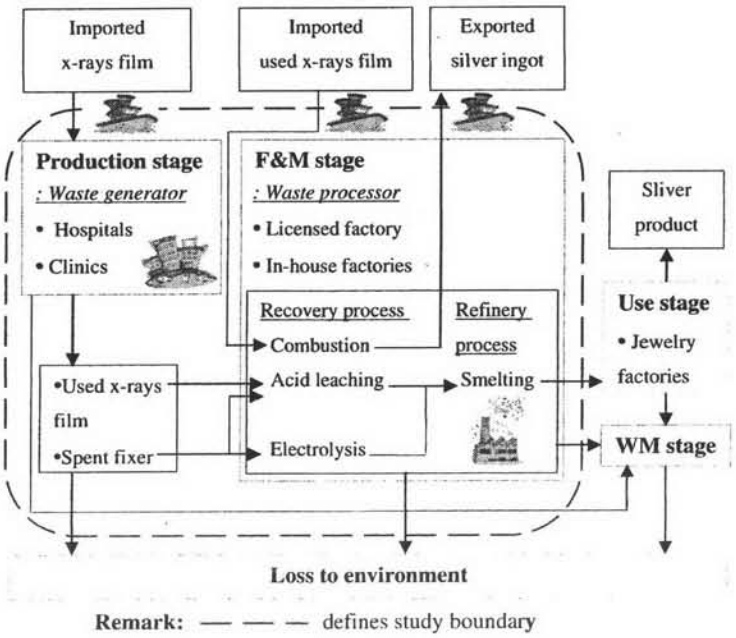

Fig. 3 Material flow analysis of silver in X-ray waste

In addition to domestic supply, used films are imported by a waste processor (WP). The price of imported used films is apparently cheaper than the domestic used film. At present, the amount of imported used films is legally limited as it is allowed for a factory test-run operation. In average, approximately 1% silver content (by weight) is found in the used X-ray film, this amount to 0.1 ton of silver as the other material input in our defined system.

After films being used for internal effect diagnosis assistance, silver becomes (primary) waste as spent photographic solution and solid sheet material. It was found that, silver, in both its metallic and compound forms, remains on the film after being developed and in the spent fixer at 55–65 and 35–45%, respectively. Finally, these wastes are generally sold to waste dealers (WDs) rather than directly to WPs for the further recovery of silver.

However, a portion of the silver sinks into the environment, through rinse water and used developer solution which are contaminated with silver during the developing process. These solutions are usually drained directly into sewerage system with silver concentrations in the range of 12–100 mg/l, which is, according to our best estimation, ca. 0.04 ton of silver.

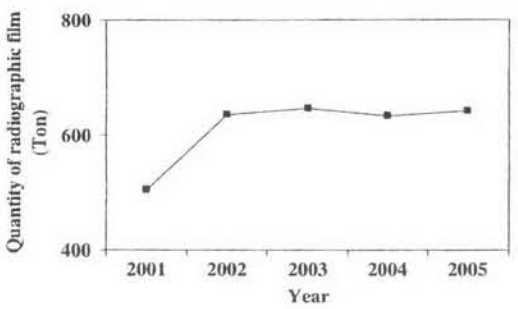

Fig. 4 Quantities of imported X-rays film from 2001 to 2005 (Thai Customs Department 2005)

F&M of X-ray waste

The used X-ray films and spent fixer enter silver recovery factories as secondary raw material. In Thailand, these kinds of factories are categorized as a typed-106 factory since they are engaged in the recycling or recovery of materials from industrial wastes and/or discarded industrial products. With a defined number of workers or horse powers, the 106-type activity becomes a factory and is controlled under certain regulations promulgated by the Factory Act B.E. 2535 (1992). To date, only a single silver recovery factory has been officially registered with the Department of Industrial Works, under the Ministry of Industry (MOI). This factory imports used X-ray films from abroad and uses them as raw materials in a combustion recovery process. Approximately, 0.09 ton of silver is recoverable by this method.

The majority of the silver recovered from used X-ray films and spent fixer solution is processed by the so-called "house" factories. These small-scale WPs

conduct their businesses without any facilities to treat their wastes and become a large group of secondary waste generators (SWGs).

Electrolysis and acid-leaching are the most commonly used silver recovery techniques. Electrolysis is an effective method for extracting silver from solution, whereas combustion and acid leaching are suitable for retrieving silver from used films. Approximately, 95–96% of the silver contained in the used film and fixer solution, which is equivalent to 12.1 ton, is recoverable.

Silver ash produced by the combustion treatment and sludge generated from the chemical leaching process are smelted and refined to obtain silver ingots, while other silver-contaminated chemicals cross the boundary into the environment or enter a waste treatment plant before release into the environment. The silver ingots are sold to domestic jewelry and silverware manufacturers.

The residual wastes, including wastewater and leached plastic sheets, which are contaminated by traces of silver, are sent for external waste management outside the system boundary. Only 40% of the wastewater has been treated in-house by neutralization or dilution prior to discharge into the environment. It was found that the amount of silver loss in the effluent is approximately 0.55 ton. Furthermore, the analysis of leached film showed that an average of 0.08% of silver by weight still retains on the film sheet.

Silver flow of X-ray waste throughout the production and F&M stages is illustrated in Fig. 5. Even total losses of 0.6 ton of silver through the biosphere in our system boundary are not comparable to the material available in the system outside. The wastes, especially the emissions from the "in-house" WPs, are classified into hazardous material categories (USEPA 2006).

Waste management

Handling waste between waste generators and waste processors

One hundred out of the entire 424 hospitals in the country, including both private and public hospitals throughout the country, were selected as the target group (National Statistic Office 2004). The data obtained from our integrated questionnaires, which focused on the hospital's management of X-ray waste, indicated that management practices differ among the hospitals. This was mainly due to the different hospitals, clinics and medical centers are under different authorities. Approximately, 87% of hospitals keep their used X-rays films for 5–10 years for their medical records; while spent fixer is reused minimal twice and collected for a number of years until it reaches a sufficient amount to be sold.

In 2002 and 2003, used X-ray films were sold approximately at a price of 839 and 777 US dollars per metric ton, respectively. The price of spent fixer was approximately 680 US dollars per cubic meter.

The X-ray WDs can be either general or juristic persons. A dealer who offered the highest price gets

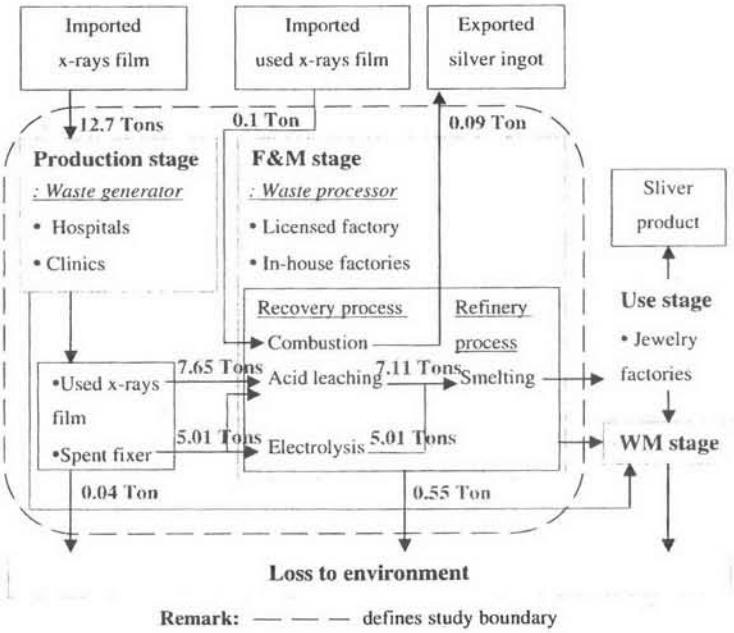

Fig. 5 Silver flow of X-ray waste in production and F&M stages. All units measured in kg Ag (from 2003 to 2004)

the X-ray films and fixer solution. In general, a bidding process is employed at a hospital where enormous amount of X-ray waste is produced to gain maximum income. These WDs are not required to provide information on their recovery processes and, especially, how the recovery of the waste is managed. Figure 6 reveals the percentages of document requirements which are a national identification card, a business establishment license, a resident registration certificate, and combinations of the afore-mentioned documents. The data showed that 44% of the studied hospitals requires merely a national identification card, and 39% of the samples requires both a national identification card and a business establishment license. Yet, only 4% of them does require all these documents.

At present, there has been no specific state notification for management of X-ray waste; as a result, it depends on individual hospitals to set up their own requirements. It appears that most hospitals have little concerns for the wastes they sell. In prequalification process of the WD, the hospitals neither take into consideration the reliability of the WP, who actually process the waste, nor require the WD to disclose their WP and the processors' operating permits. This means that no information about these WP is officially available. Therefore, the concern of hospitals for their X-ray waste seems to end up after the bidding process end because the hospitals have no clues to which their X-ray wastes are transported and how the wastes are subsequently processed.

Problems of X-ray waste management

Based on our analysis, it was found that there are intrinsic problems occurred in a system. Figure 7 shows the relationship between an X-ray material flow and key stakeholders. The figure depicts five major stakeholders: (i) X-ray film and fixer suppliers, (ii) primary X-ray WGs, (iii) X-ray WDs/vendors, (iv) X-ray WPs or secondary X-ray WGs, and (v) X-ray waste regulators (WRs).

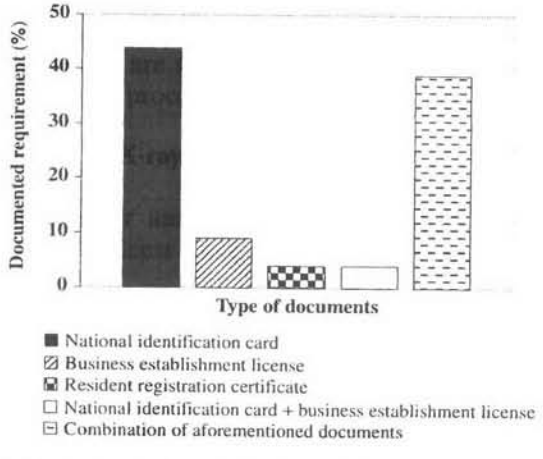

Fig. 6 Percentages of required documents

First of all, for the supply side, there is adequate statistics from the Department of Customs, under the Ministry of Finance; as the materials are all imported into the country. The mass quantity and the names of importing firms are well-documented and the information is available for public.

Secondly, the PWGs, which can be divided into two groups: Large PWG and Small PWG. The Large PWG, i.e., hospitals or medical services, account for a large portion of X-ray waste quantity. In general, they have been subjected to some regulations endorsed by the Public Health Act B.E. 2535 (1992) and issued by the Ministry of Public Health (MOPH). Nevertheless, up to the present, there has not been any specific rule for the control of X-ray waste from Large PWG issued by MOPH.

The Small PWG, i.e., factories and some photo shops that use X-ray films in their production processes, are small X-ray waste producers. X-ray waste from these factories is currently under the control of MOI by use of the Factory Act B.E. 2535 (1992). Yet, there is no control for the photo shops.

Thirdly, the X-ray WPs, i.e., used film and spent fixer recycling factories, which are, on the other hand, the SWGs. As it was previously described, only a single WP is registered and controlled by MOI via the enforcement of the Factory Act B.E. 2535 (1992); while a number of "house" factories remains unknown.

It appears that the major feed raw materials for a silver recovery factory would be collectable from the medical services within the country. But, actually, the X-ray waste of domestic origin has hardly ever processed at the only one licensed factory in Thailand. This factory has to import used X-ray films for its recycling operation. It is obvious that a loophole exists in the state control system.

The X-ray waste from industrial operations, both as PWG and SWG (or WP) is legally defined as "industrial hazardous waste" according to the Ministerial Notification No. 6 B.E. 2540 (1997) of the Factory Act B.E. 2535 (1992). This Act requires a factory that produces and/or recycles its X-ray waste to apply for an operating permit for their factories and a waste evacuation license from the MOI. However, this law can only be enforced on a factory; but not applicable to the other major WG (i.e., hospitals), which are regulated by the Public Health Act B.E. 2535 (1992) and to a

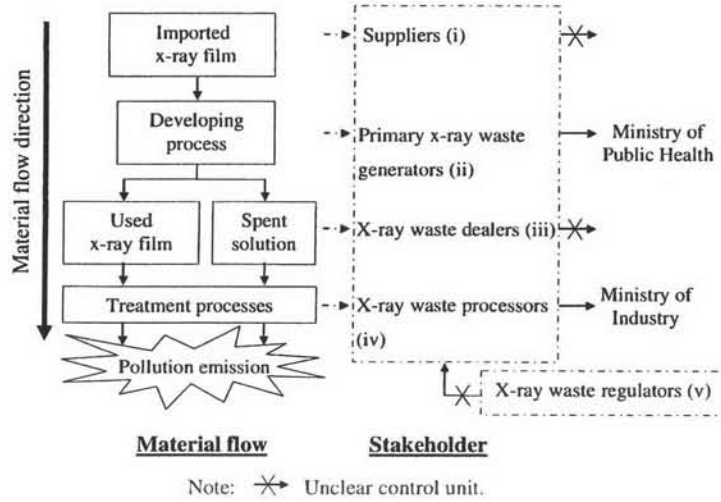

Fig. 7 Relationship between X-ray material flow and stakeholders

"house" factory. The "house" factory is not considered as "a factory" under the Factory Act B.E. 2535 (1992), unless it utilizes power equal or more than 5 horse powers and/or employs equal or more than seven workers.

Fourthly, the X-ray WDs, who actually transfer wastes from the generators to the processors, are free waste traders; no government body is designated to overlook these dealers. As a result, it is very difficult to identify where the waste commodity is distributed. Thus, it is not possible to locate where the waste is delivered and to specify who manages it.

Finally, the WRs, there occurs both regulatory gaps and overlapping jurisdictions among government authorities; this results in a non-systematic management of X-ray in Thailand. Hospitals as Large PWG, which are affiliated to and/or under a control different state agencies, are lacking of close cooperation to set up measures to control their X-ray wastes, such as defining of waste (to be hazardous or non-hazardous), separation and collection procedures, rules to select the WD and WP, and monitoring measures.

At present, it seems that there is one direction of material flow without any monitoring system. Pollution originated from silver recovery processes continues to release into the environment without awareness or proper treatment. Official records of the X-ray waste are not sufficient for planning of a proper management of the waste.

Future prospects for X-ray waste management

In Thailand, the existing measures are insufficient for controlling X-ray waste. In order to achieve the goal of complete waste management, silver as a hazardous element should be strictly monitored and tracked from the generation points to their ultimate disposal sites as proposed in Fig. 8. Pollution prevention guidelines in the form of a fact sheet were then developed to manage silver-contaminated wastes for businesses that produce the wastes. The main subjects covered in the fact sheet are type of X-ray waste, lists of management and disposal options, manifest system, and name lists of WD and silver WP in Thailand.

Type of X-ray waste

X-ray waste consists of used X-ray films, spent fixer, spent developer, water rinse and chemical vapors. The used X-ray films and spent fixer are considered as hazardous wastes due to their high silver content.

Lists of management and disposal options for spent photographic solution and used films from waste generators to waste processors

Because silver content in both spent fixer and used film can be recycled, the WGs should handle these wastes separately from other wastes. For instance, the fixer should not be mixed with spent developer.

Of importance is the selection of the X-ray waste management company because their liability should not end up when the waste is evacuated from the hospital facility. Guidelines have been established for choosing a company for an off-site disposal of X-ray waste. For example, the recyclers have to apply for a permit from the MOI. In addition, they would have to treat the wastes generated from the recycling process prior to release it into the environment.

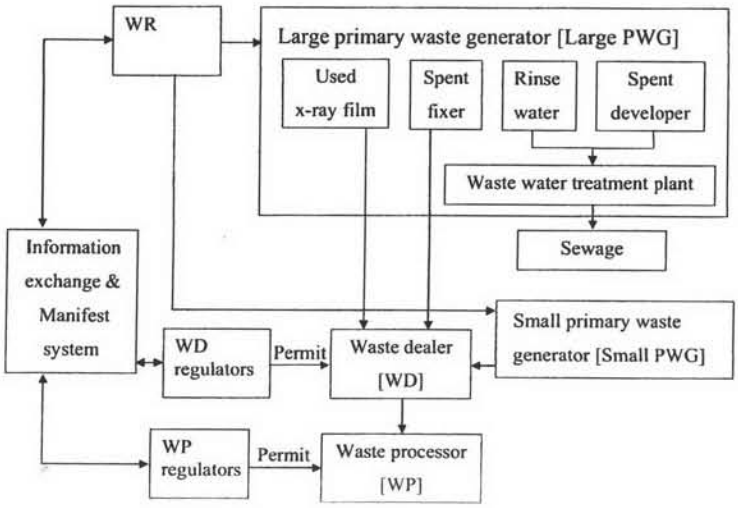

Fig. 8 Proposed X-ray waste management system

Manifest system for X-ray waste

A manifest system for X-ray waste is needed to control and to monitor the waste. A manifest paper is a management tool to keep track on the silver-contaminated hazardous waste during transportation. The manifest serves as a legal document for hazardous wastes that would not be able to be shipped off-site without it. The WR should establish the linkage with each other to jointly and uniformly monitor the waste.

Name lists of dealers and silver waste processors in Thailand

Both WD and WP have to register with the regulatory bodies. Fundamental information of them such as name, address, a silver recycling method and a waste treatment process, should be publicized to facilitate and to normalize a selection for WD. Only a dealer associated with licensed silver recycler should be allowed to enter the bidding process of the WG.

The WR might use the Hospital Accreditation (HA) standard as an incentive tool to help controlling X-ray waste by adopting the fact sheet as a specification for X-ray waste management. HA certification system plays a key role for improvement of hospital quality by increasing both efficiency and competitiveness. Waste management is mentioned as one aspect of this standard; however, its specifications have not set up yet.

Conclusion

X-ray waste management in Thailand involves a number of parties: the WGs, the WDs, the WPs and the WRs. Inadequate regulatory attention is paid on X-ray waste management. A material flow analysis was used for investigation of the silver loss to the environment. It was found that a considerable amount of silver has been released into the environment. The discharge mostly comes from the small WPs, which are not registered and licensed. These "house" factories exempted environmental rules and regulations. The concrete rules for the WPs are yet to be formulated. The fact sheet for management X-ray waste proposed includes necessary measures to keep the X-ray waste from on-going deterioration of the environment.

Acknowledgments Special thanks are extended to the Cleaner Technology Internship Program 2006: Thammasat University Node for financial support.

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Radiographic film waste management in Thailand and cleaner technology for silver leaching

P. Khunprasert [a], N. Grisdanurak [b,*], J. Thaveesri [c], V. Danutra [a], W. Puttitavorn [d]

[a] National Research Center for Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok 10330, Thailand
[b] Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Klong-Luang, Pathumtani 12120, Thailand
[c] Department of Industrial Works, Ministry of Industry, Bangkok 10400, Thailand
[d] The Institute of Environmental Research, Chulalongkorn University, Bangkok 10330, Thailand

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Abstract

In Thailand, a large amount of radiographic film waste is generated in hospitals. Fixer and developer solutions removed approximately 35–45% of the sensitive silver compounds from the films, depending on the object exposed. Solutions are reused twice, while used films are kept for the records for more than 5–10 years. After that, these wastes are sold to dealers. More than 90% of the dealers are not officially registered. Wastes are delivered to in-house factories to recover silver either by electrolysis, acid leaching (HNO_3) or combustion process. Most waste processors are not really concerned with handling the wastes. Highly toxic chemicals are generally spilled and discharged into the environment. The cleaner technology concept of silver leaching from radiographic film was investigated using weak acids such as acetic, oxalic and malonic acids. The tests were carried out under low temperature conditions.

An oxalic acid solution at 5% (w/v) provided the best leaching condition at 100 °C for 20 min. This achieved 100% silver leaching from the films. The obtained silver was in its metal form and ready for ingot production. Following this, a fact sheet on the waste management of radiographic film waste was created to reduce the risks of spills and leakages of hazardous silver into the environment.

Keywords: Radiographic waste; Silver removal; Waste management

1. Introduction

To date, only a few articles have been reported on silver cycles [1,2]. They have discussed the presence of silver cycles in commodities of the industrial sectors rather than those from medical usage. The stock and flow of silver with regard to photographic film processing have been a concern in Thailand's effort to improve its waste management. Radiographic film is a polyester sheet coated on both sides by radioactive material, which is sensitive to light. It is used for industrial purposes and medical and dental services for some investigations. Approximately 2 billion radiographs are taken around the world each year, including chest X-rays, mammograms, CT scans, etc. Traditionally, 94–98% of X-ray films are used in medical services [3]. Several waste streams are generated in hospital radiology departments, such as wastewater containing photographic chemicals, scrap films such as those purged from old files, or chemicals and silver removed from the film generated from poor photographs during processing, fixer solutions, and spoiled chemicals.

The wastes described previously are classified as "hazardous" due to their heavy metal contents. Like other countries, Thailand has recognized that the wastes from the production and formulation of photographic chemicals, and the processing of the material are defined as hazardous wastes by the Notification of the Ministry of Industry No. 6 [B.E. 2540 (1997)] issued pursuant to the Factory Act B.E. 2535 (1992) in Chapter 4, Section 20 in Ref. [4]. Even though it has been legally

* Corresponding author.
E-mail address: gnurak@engr.tu.ac.th (N. Grisdanurak).

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recognized as a hazardous waste for several years, silver concentration amounts from 2000 to 6000 mg/l have been found in fixer solutions [5]. In addition, more than 60% of the silver remains coated on used film after it is developed.

Existing technologies used for silver recovery are precipitation, ion exchange [6,7], and electrolysis [8]. Some hospitals provide an electrolysis silver recovery service for the on-site treatment of silver recovery. Many researchers have studied options for silver recovery from developing solutions, such as adsorption by activated carbons [9], chitin [10], etc. Up to our knowledge, there is little information on retrieving silver from used films. In Thailand, in particular, used film sheets have been managed carelessly. The main subjects covering radiographic silver waste in this paper are as follows:

- The present situation and a material flow analysis.
- Silver recovery techniques.
- Problems and a fact sheet on waste management.

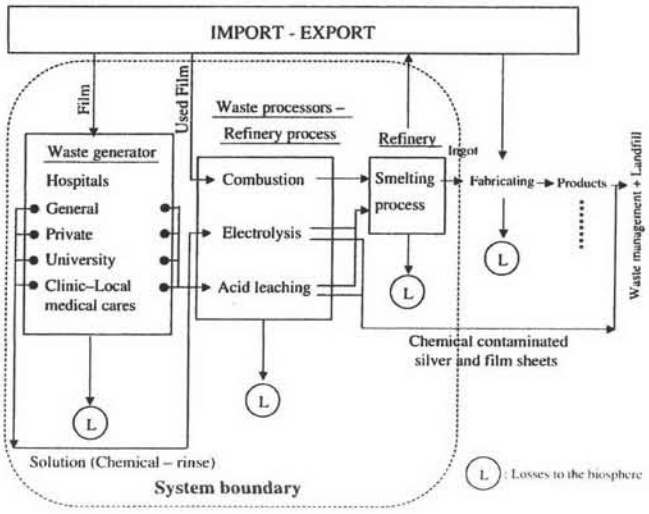

Fig. 1. Material flow of silver in radiographic hospital waste.

2. Current situation of radiographic silver waste in Thailand

A Substance Flow Analysis (SFA) [2] was used to apply the concepts of industrial ecology to study how materials and energy flow into, throughout, and out of the system. This tracking system assists the evaluations of effects to the society, the economy, and the environment from extraction through production, consumption, and finally disposal. An equation of the conservation of mass is used to describe the silver substance flow in a limited boundary. This is to access the flow patterns of the silver waste cycle; to determine the amounts that are recovered and lost as waste; and to establish the amounts entering the reservoirs.

The conservation of mass is described by a basic substance flow equation:

$$\frac{dF}{dt} = \sum F_{input} - \sum F_{output} + \sum (S_t - S_{t-1}) \quad (1)$$

where F refers to material flow into and out of each hospital, inside the control volume, and S designates the stock of material retained or depleted from the reservoir over the time period. Film consumption data for each hospital are documented, however, the stocks are not documented; but there should not be much difference between each year since the stocks depend upon the limited space in each hospital.

Fig. 1 illustrates the silver waste life cycle as treated in this work, including the sub-processes, and the material flows linking them together. Silver used in medical services appears on the X-ray film. Currently, there are no film manufacturers in Thailand. Therefore, all the film used in Thailand is imported. Film is distributed to several kinds of hospitals, such as general, private and university hospitals, which are managed by different policies and stakeholders, including the Ministry of Industry, Education, and Public Health. After in-house image developing, silver becomes waste in both the solution and solid sheet material. Waste collection procedures differ from hospital to hospital, and between the waste types. The wastes are usually kept for a certain amount of years, and later sold to waste processors for further recovery. At this point, some used film is imported to Thailand to recover its silver. Several techniques, such as electrolysis, acid leaching, and combustion, are utilized to obtain silver complex. Silver in chemicals is collected by electrolysis, while silver in used film is retrieved by combustion and acid leaching. Silver complex is sold to a smelting process to obtain ingots, while contaminated silver chemicals cross a boundary for other treatments. Ingots are then ready to be sent out from the studied boundary for fabricating and manufacturing.

Under steady-state conditions within the one year period of consideration, the accumulation term approaches zero. The net accumulation of material would be equal to the summation of silver flowing into the system minus silver flowing out from a defined control volume. If one were to consider the years 2003–2004, Eq. (1) could be written as follows:

$$F\,\text{silver} = \sum F_{input\ (2004)} - \sum F_{output\ (2004)} + \sum S_{(2004)} - \sum S_{(2003)} \quad (2)$$

2.1. Radiographic silver waste generator

The Customs Department (Thailand) has the duty of recording the amount of X-ray film that is imported; data on this are presented in Fig. 2. The annual imported amount increased and then remained stable at around 630–640 metric tons of film. According to the composition of silver content in the film as shown in Table 1, an approximate amount of 13 tons of silver enters the country's environmental cycle each year.

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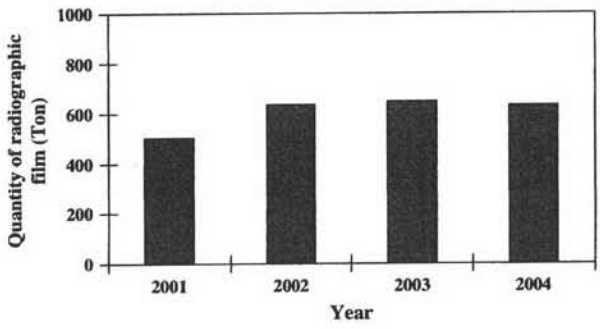

Fig. 2. Quantity of imported X-ray film from 2001–2004 [17].

According to our analysis, an average of 35–45% of the silver compounds are removed from the film after it is developed. Similar to our results, the Colorado Industrial Pretreatment Coordinators Association, 2004, disclosed that the remaining silver on film was about 60% [11]. Rinse water, usually discharged directly into hospital sewage, is found to have silver contamination, in the range of 12–100 mg/l, from the radiographic laboratory effluents of many hospitals. According to the concentration which is higher than 5 mg/l [12], it falls into the hazardous material category.

2.2. Radiographic silver waste processor

Used film and developing solution waste are collected and kept in the hospital area for their annual sale to waste dealers. Wastes in solution form (fixer and developer) are kept for a one-year period; while approximately 87% of hospitals keep used X-rays films for 5–10 years depending on the medical treatment criteria (for personal records) and the size of the collection area. Waste processors of photographic waste are categorized as type 106 – recycle, reuse, or recovery factories – based on the attached list of the Ministerial Regulation B.E. 2535 (1992), according to the Factory Act B.E. 2535 (1992) [4]. The factories that accept these wastes must be registered officially.

Table 2 shows the number of waste processors for silver recovery. Recently, only one silver recovery factory has been authorized by the Department of Industrial Works (DIW). This factory uses a burning method followed by a melting process.

Table 1
Silver content in materials

Material	Silver content per unit material (g Ag/m^2)	Total silver (kg Ag)
Original X-ray film	4–6[a]	12 700[c]
Used X-ray film	3.0–3.5[a]	6980–8320[d]
Solution (fixer + developer)	around 2000–6000 mg/l[b]	

[a] Material sample is digested with HNO_3 and determined by AAS.
[b] Solution sample is directly measured by AAS.
[c] Total silver is estimated from 2% Ag on amount of imported X-ray film in 2004.
[d] Total silver is estimated from 1.1 to 1.3% Ag on amount of imported X-ray film in 2004.

Table 2
Factory lists managing radiographic wastes

Process	Number of factory	Remark
Combustion/burning	1	In import–export zone
Electrolysis	17	
Acid leaching	8	

However, this plant is located in an import–export zone, meaning that only imported used film can be managed by it. The remaining 25 waste receivers are not registered. They all carry out in-house operations, either electrolysis or acid leaching processes. Factories with the electrolysis process recover silver from the developing agent waste, while factories with acid leaching operations recover silver from used film. However, they lack proper waste management systems. Fig. 3 shows the accessible areas of several in-house waste processors.

Leakage and spills were generally observed during the walk-in process. The rinse water chemical after silver recovery might contain traces of silver, therefore further treatment would be required. About 60% of the rinse water has been delivered to the treatment plant outside the boundary, while the rest is treated in-house by the neutralization or diluting process and then dumped into the environment. Our investigation found that approximately 5400–8700 mg of Ag/l was present in the processor effluents.

Silver complex from the recovery process is passed through a smelting step for remolding into an ingot. Afterwards, it is sold to fabricating manufacturers or exporters. Ingots refined from the import–export zone are entirely exported, while the ingots refined in in-house factories are sent to be fabricated for hand-made domestic products.

Losses to the biosphere can be calculated from the mass balance equation. Fig. 4 presents silver flows in medical care services and waste processors. Approximately 91.8% has been recovered from the radiographic film and solution process. From the analysis of processed film after acid leaching and electrolysis, some silver was found on the film sheet at an average of 0.08% wt. However, these chemical contaminated silver and film sheets were sent for waste management outside the system boundary. Even though the losses through the biosphere in our system boundary are not significantly compared to the system outside, the concentrations from each step seem to be over the standard concentration [12]. The emission from the in-house waste processors was found to be high and should be taken into consideration for the purpose of pollution prevention.

3. Silver recovery techniques

3.1. Present recovery techniques

Two typical ways to recover silver from used radiographic films are combustion technology and the acid leaching process. The used film is incinerated at high temperatures

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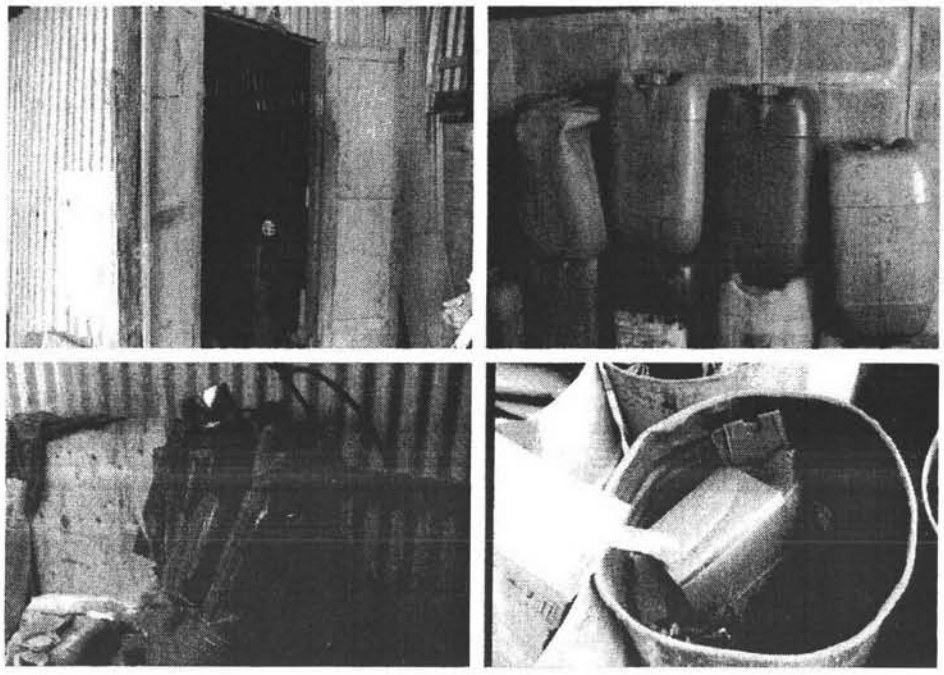

Fig. 3. In-house waste processor for silver recovery.

(>980 °C) in the combustion process and silver is recovered from ash by smelting and refining processes. Generally, the yields from the burning process are less than 95% [13,14]. In the acid leaching process, used film is submerged into a strong acid solution. Several chemicals, such as cyanide solution, ferric chloride, hydroxide, nitric acid, etc., have been used. A yield for the chemical leaching method is 99% [15]. It is operated as an open system at 70–80 °C, with a retention time of 30 min. Both processes have some environmental disadvantages.

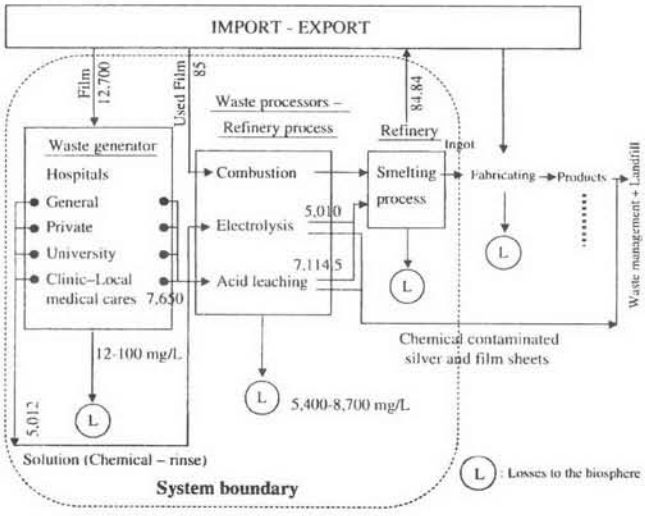

Fig. 4. Silver flows in a hospital waste generator and in-house recovery. All units measured in kg Ag (in the year 2003–2004).

3.2. Proposed cleaner technology approach for silver recovery

In order to reduce the usage of high temperature conditions and highly toxic solutions, we investigated how to use a weak acid as a leaching agent to remove silver. Acetic, oxalic, and malonic acids were used in this work. The investigation was performed through the leaching process on the effects of acid, temperature, and aging time. Used radiographic film chips of the same size were weighed and extracted under refluxing at 60–100 °C with 1–5% (w/v) acid solutions for 10–120 min. Afterwards, the films and sludge were separated out of the solution by filtration with 42 filter paper, Ashless (Whatman). The entire procedure is summarized as shown in Fig. 5.

3.2.1. Analytical method

Sludge was dried at 105 °C for 2 h, cooled down to room temperature in a desiccator and burnt in a furnace at 500 °C for 3.5 h. The ash was digested with microwave digestion by 10 ml of HNO_3 until the solution became clear. The silver concentration in the solution and sludge solution was measured by Atomic Absorption Spectroscopy (AAS). The silver concentration in the solution after the leaching process was measured by AAS. Silver sludge morphology was tested using Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) Linkisis Series and X-ray Diffraction (XRD).

3.2.2. Results and discussion

A size of $1 \times 1\ cm^2$ of radiographic film chip was used to avoid the attachment problem during the test run. In this study, increasing acid concentrations of 1–5% (w/v) were used. It

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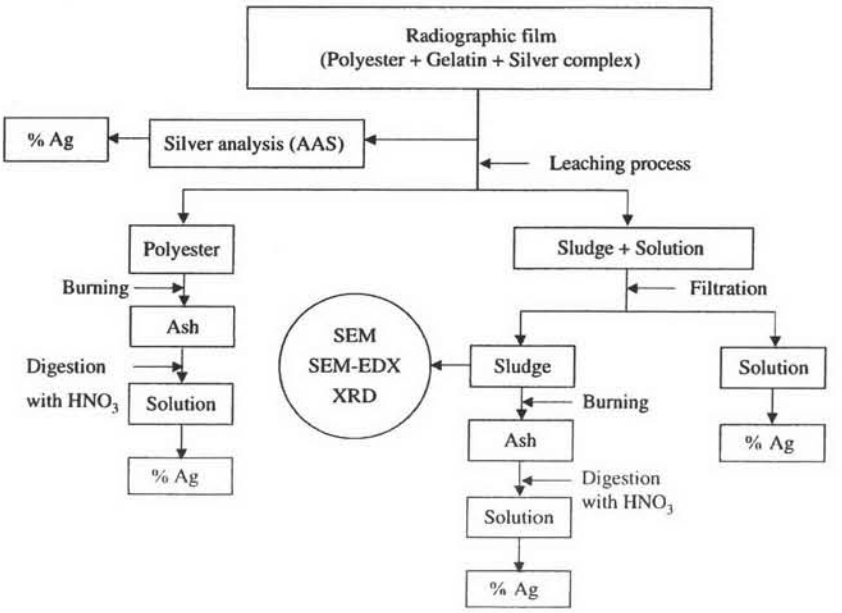

Fig. 5. Experiment schematic flow.

was observed that the removal efficiency could be enhanced by increasing the concentration of all the acids, as shown in Fig. 6(a). Oxalic acid provided the highest silver removal compared to malonic and acetic acids. Several duplication tests were done for each of the conditions; it was found that at 100 °C, 20 min and 5% oxalic acid concentration, there was nearly 100% removal. The effect of temperature on the extraction method for 10 min at 5% (w/v) acid solution is shown in Fig. 6(b). The efficiency of the extraction rate for each chemical increased strengthening of the temperature. However, some of the constraints should be addressed in order to recycle both film residue and solution. An example is that the temperature should not be higher or close to the melting point of the film. Therefore, as a further suggestion, 100 °C should be sufficient. As shown, there was not much extraction at temperatures less than 80 °C. It was then expected that the temperature was not high enough to dissolve the gelatin. However, at 90 °C or higher, the reaction worked well.

From the experimental results, the extreme conditions in which silver is leached out of film, as shown in Fig. 7, are at temperatures of 90 and 100 °C. The effect of the heating time on the extraction process was investigated at 10–120 min. This factor is related to the temperature. Certainly, the higher temperature provided more removal efficiency. However, the condition at 100 °C, supported by results of the leaching process, can be carried out with a short retention time. The best removal efficiency conditions, which provide the highest potential of leaching (>99% efficiency removal), are at 5% (w/v) acid solution at 100 °C for about 20 min.

A characterization of residue of the leaching process at the optimum condition was performed. XRD, SEM and EDX were used. The XRD patterns of silver sludge from the leaching process were inspected. The major diffraction line of the residue sludge was presented at 38 (111), 44 (200), 64 (220), 77 (311), and 81 (222) degree 2θ, corresponding to the silver element fingerprint. Other kinds of silver complexes such as silver oxalate, and explosive materials could not be found. Fig. 8 shows the silver particles with a magnification of 3000, loaded onto the plastic film layer (a) and silver waste after leaching (b), respectively. Using an EDX, the particles present on the film were detected as

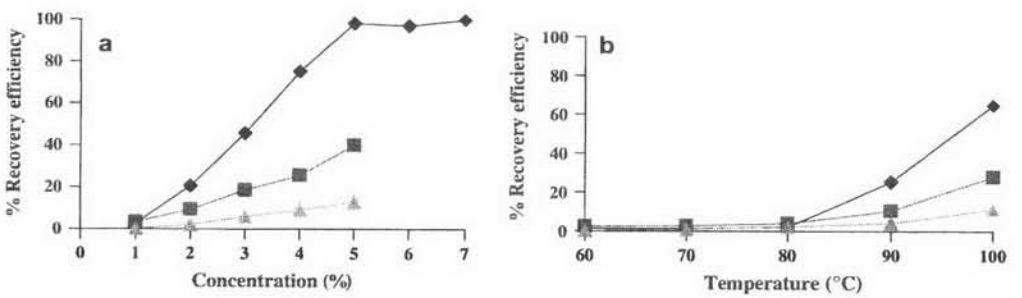

Fig. 6. Recovery efficiency (%) from the extraction process of 1 cm^2 processed film by (◆) oxalic acid, (■) malonic acid, and (▲) acetic acid. (a) Extraction process at 100 ° for about 20 min by refluxing with various acid concentrations. (b) Extraction process by refluxing with 5% (w/v) acid concentration for about 10 min at various temperatures.

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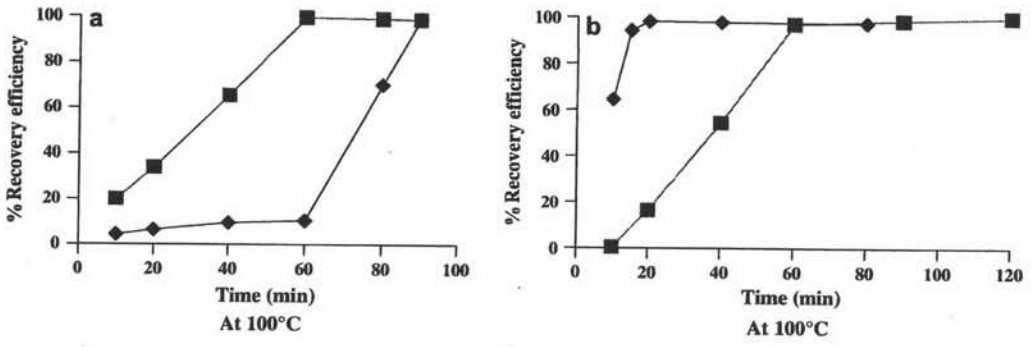


Fig. 7. Recovery efficiency (%) from the extraction process of 1 cm^2 processed film by refluxing, with various retention times (◆) 1% (w/v) oxalic acid, (■) 5% (w/v) oxalic acid.

silver element. Silver particles first appeared in a clearly spherical form covered with gelatin. After treatment, acid dissolved the gelatin by breaking down the cross-link network of the gelatin. As a result the gelatin became flaky. However, the silver remained in the same shape covered with the flaky gelatin. These results confirmed that oxalic acid solution leaches silver out from the sheet without any reaction with the silver. In addition, this acid solution can be reused for this process several times.

3.3. Comparison of technologies

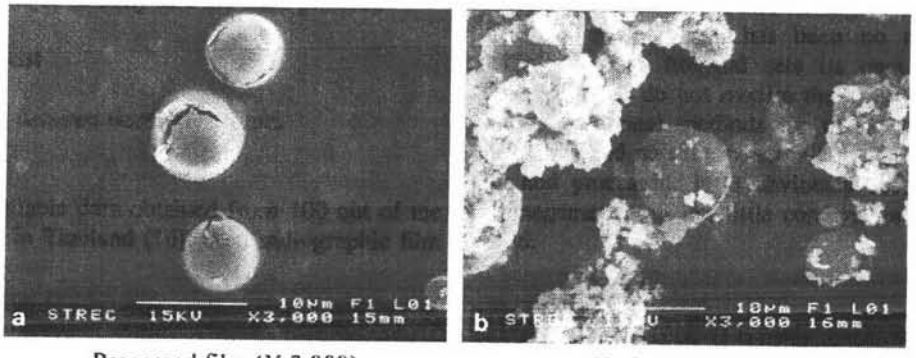
In this section, the lists of advantages and disadvantages for available technologies and our study are tabulated in Table 3. Temperature, toxicity, and other operating conditions were considered. According to the operating phase, it is obvious that all of them provide similar excellent silver removal; however, oxalic acid leaching has a higher leaching potential than the other two in terms of toxicity and the final product.

4. Waste management

4.1. Handling waste between waste generators and waste processors

Based on the available data obtained from 100 out of the entire 424 hospitals in Thailand [16], used radiographic film was sold at approximately 839 and 777 dollars per metric ton, for the years 2002 and 2003, respectively. For radiographic solutions, only used fixer was sold because it contained a high silver content, while used developer and water rinse were discharged into a hospital's wastewater treatment plant. The price spent on fixer in both years was approximately 680 dollars per cubic meter. A bidding process is generally used at each hospital to obtain the highest income.

The waste dealer of radiographic waste can be either a general or juristic person. Generally, hospitals have not required specific proof from waste dealers. The presence of an identification card might be enough. Fig. 9 discloses the percentages of required documents. A copy of an identification card, a copy of a business permit, and a copy of a resident registration are required at 45%, 9%, and 4%, respectively. Only 4% of the hospitals require all three documents. Table 4 summarized the present measurements and problems of each hospital with regard to the management of the radiographic waste. Because there has been no regulation announced officially, each hospital sets its own requirements. Some hospitals also do not require the waste dealers who disclose their operational methods for their waste processors. Most hospitals had no clue where all wastes were being delivered to and processed. It is obviously seen that hospital waste management staff has little concern for the waste after being sold.



Processed film (X 3,000) Sludge (X 3,000)

Fig. 8. Silver particles on processed film and sludge from the extraction process by refluxing with 5% (w/v) oxalic acid at 100 °C.

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Table 3
Lists of advantages and disadvantages for available silver removal techniques

Criteria	Combustion	Acid leaching	
		HNO_3, cyanide solution	This work: oxalic acid
Temperature (°C)	>980	~70–80	~90–100
Operating condition	High efficiency	High toxicity	Lower toxicity
	Short retention time	High efficiency	High efficiency
		Short retention time	Short retention time
		Able to be reused	Able to be reused
Emission	High CO_2 air emission	Low CO_2 emission	Low CO_2 emission
		Acid vapor emission	Acid vapor emission
Product	Sludge containing silver complex, and require a smelting process	Silver complex, such as silver nitrate and silver cyanate, requires electrolysis for a further process.	Sludge containing silver element with gelatin, and simple for a smelting process.

Some waste dealers do not even have a commercial register authorized by the Ministry of Commerce, Thailand (MOC). For those who have been registered with the MOC and report to the office; however, the recorded information is not linked to the waste processor. Additionally, the management system after selling is not disclosed. These are some of the general misconceptions of radiographic waste management.

4.2. Problems of radiographic waste management

From the survey data about the radiographic waste management system, it was found that there are many drawbacks, they are as follows:

(1) There are too many waste dealers and waste processors to cope with the radiographic waste generated in Thailand; however, it is not clear where all the used radiographic waste goes and who manages them.
(2) In addition, there are some unofficial waste processors of silver wastes, who are not concerned about whether the treatment is green or not. This presents significant potential hazards to humans, especially to the workers and the environment when untreated pollutants are emitted.
(3) There is a lack of a manifest system of radiographic waste along the waste stream. It is complicated for the regulators to control and monitor the waste.
(4) Radiographic waste is under the control of many authorities. They set different measurements to deal with the waste, such as different definitions of waste (hazardous and non-hazardous wastes), management procedures, etc. Moreover, the regulators of each section lack cooperation, which leads to a gap at the regulatory level, especially towards the waste dealers.
(5) The only official waste processor imports all the raw materials, the used X-ray film, from another country to treat or recover silver. The transport of hazardous waste from foreign countries for treatment in Thailand seems to be a growing trend. That means all of the pollution that occurs after treatment remains in our nation.

5. Future prospects for radiographic waste management

In order to achieve the goal of used film waste management, silver hazardous wastes should be strictly monitored and tracked from the point of generation through to their ultimate disposal. In addition, better recovery techniques are required.

A management tool is to keep track of this hazardous waste through a shipping document called a hazardous waste manifest. Hazardous wastes may not be shipped off-site without a manifest and each manifest serves as a legal document. In general, this manifest does not cover the waste generated in hospitals. A single manifest typically consists of six copies, each designated for specific destination. This distribution of copies ensures that all parties involved (i.e. the hospital as a waste generator, waste dealer, waste processor, and the DIW) receive matching copies confirming the proper transport and disposition of hazardous waste.

The flow of material and the manifest is shown in Fig. 10. The hospital (the waste generator) retains copy 1 to be rechecked with manifest copy 5 after the wastes are delivered. The waste transporter retains copies 4–6 with the shipment. Upon arrival with the shipment at the treatment, storage, and

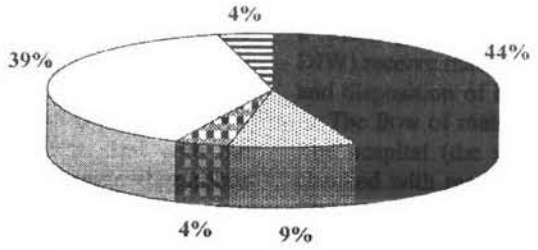

Fig. 9. Requirement percentage of each document type: ■ a copy of an identification card, ▨ a copy of a business permit, ▣ a copy of a resident registration, □ a copy of an identification card + a copy of a business permit, ▤ a copy of an identification card + a copy of a business permit + a copy of a resident registration.

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Table 4
Present measurements and problem for radiographic waste management of waste generators

Type of hospitals	Regulator	Process	Problem
Public hospitals	Ministry of Public Health	Transferring an administrative duty to finish in each hospital. The hospitals set their regulation for the management radiographic waste.	- Lack of standard measurement to manage radiographic waste radiographic waste. - Lack of direct authority to control.
	Bangkok Metropolitan Administration (BMA)	Hospitals set their regulations for the management radiographic waste. They just report to the BMA, after finishing the process.	- The waste management policies enacted to manage this waste are different.
	Ministry of University Affairs	Hospitals set their own rules but do not report to anyone.	
	Other authorities	NA	
Private hospitals	–	The hospitals set their own regulation for the management radiographic waste.	

disposal facilities (TSDF), the transporter retains copy 4 and submits copy 5 to hospital waste generator and copy 6 to the DIW. The DIW would then be able to verify the amount of waste generated by the hospitals and waste processors by manifest copies 2 and 6. The DIW should provide the linkage with the Department of Public Health (DPH) to monitor the amount of imported film. Moreover, waste transporters and processors should be strictly registered under the law.

5.1. Conclusions

Used radiographic film waste management in Thailand involves many parties: the waste generators, waste dealers, waste processors and waste regulators. Recently, serious attention has not been placed on the management part of the equation. A material flow analysis was used to investigate the loss to the environment. It was found that a huge amount of silver has been distributed to the biosphere. The releases are mostly at the level of the waste processor units, which are in-house factories that are not officially registered. The use of weak acids to leach silver from the processed film was studied. A high efficiency of silver removal by oxalic acid could be obtained within moderate conditions. Oxalic acid dissolves gelatin without reacting with the silver to form its complex. This provides for the simple separation of silver waste and allows for the benefit of reuse. Finally, prospective suggestions for the management of radiographic waste are proposed in the form of a simple manifest and proper monitoring system.

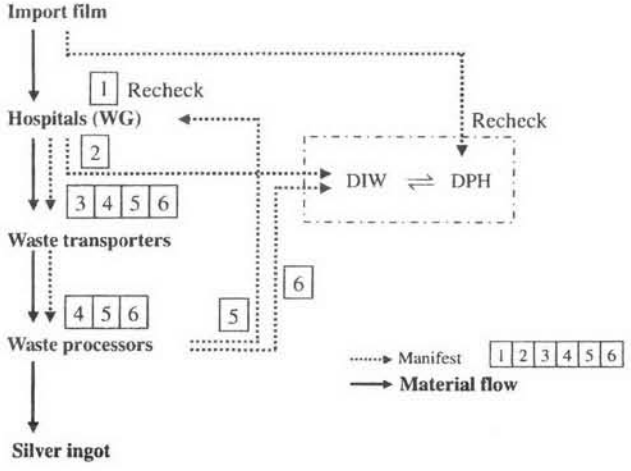

Fig. 10. The use of a manifest to track hospital radiographic waste flow.

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BIOGRAPHY

Miss Pattamawan Khunprasert, was born on February 2, 1975 in Samutprakarn, Thailand. She finished her secondary school from Non-Formal Education Center, Bangkok. After that, she joined and graduated in major of Science-Chemistry, Faculty of Education at Srinakharinwirot University and graduated in 1994. Afterwards, she enrolled in Master's degree in Environmental Technology, Faculty of Energy and Material, King Mongkut's University of Technology Thonburi in 1998.

In 1999, she worked at Technical Provision and Planning Division, Department of Public Cleansing, Bangkok Metropolitan Administration. She moved to work at Technical Provision and Planning Division, City Planning Department, Bangkok Metropolitan Administration in 2000. In the same year till now, she has been Scientist at Hazardous substances Information Center, Hazardous Substances Control Bureau, Department of Industrial Works, Ministry of Industry.

In 2003, she started her Ph.D. degree in International Programs in Environmental Management, Chulalongkorn University and completed the program in May 2007.

During her Ph.D. study, she was accepted as an oral presentation in The First International Conference - Environmentally Sustainable Development, Pakistan, 2005 and Southeast Asia Regional Symposium on Chemical Engineering "New Trend in Chemical Engineering", Vietnam in the same year.

Before she accomplished her Ph.D. degree, her research work was published in the international journals; Clean Technology and Environmental Policy volume 9, no. 2, page 93-101, 2006, Journal of Cleaner Production, available online at http://www.dx.doi.org./10.1016/j.jclepro.2006.06.010..