



## CHAPTER 2

### THEORY BACKGROUND AND LITERATURE REVIEW

#### 2.1 Steel mills in Thailand

There are 150 steel product manufacturers with a combined annual production capacity of 20 million tons, and a combined workforce of 20,000. The majority of industry is downstream manufacturers turning out long products, mainly reinforcing bar, wire rod and section for the construction industry. Many of them import scrap iron for forging into billets that are re-rolled into steel bars. For flat products, Sahaviriya Steel Industries is the country's first hot-rolled steel sheet manufacturer established after the Thai Government liberalized the industry in 1994. The company uses imported steel slabs as raw material. Development of further upstream production for basic products such as pig iron and sponge iron and intermediate products such as billets, blooms and slabs is unlikely to occur in Thailand in the near future. This is due to the country's existing constraints like unavailability of large capital funds, inadequate supplies of iron ore, the high cost of fuel for smelting, and inadequate infrastructure [U. S. Department of Commerce, 2000].

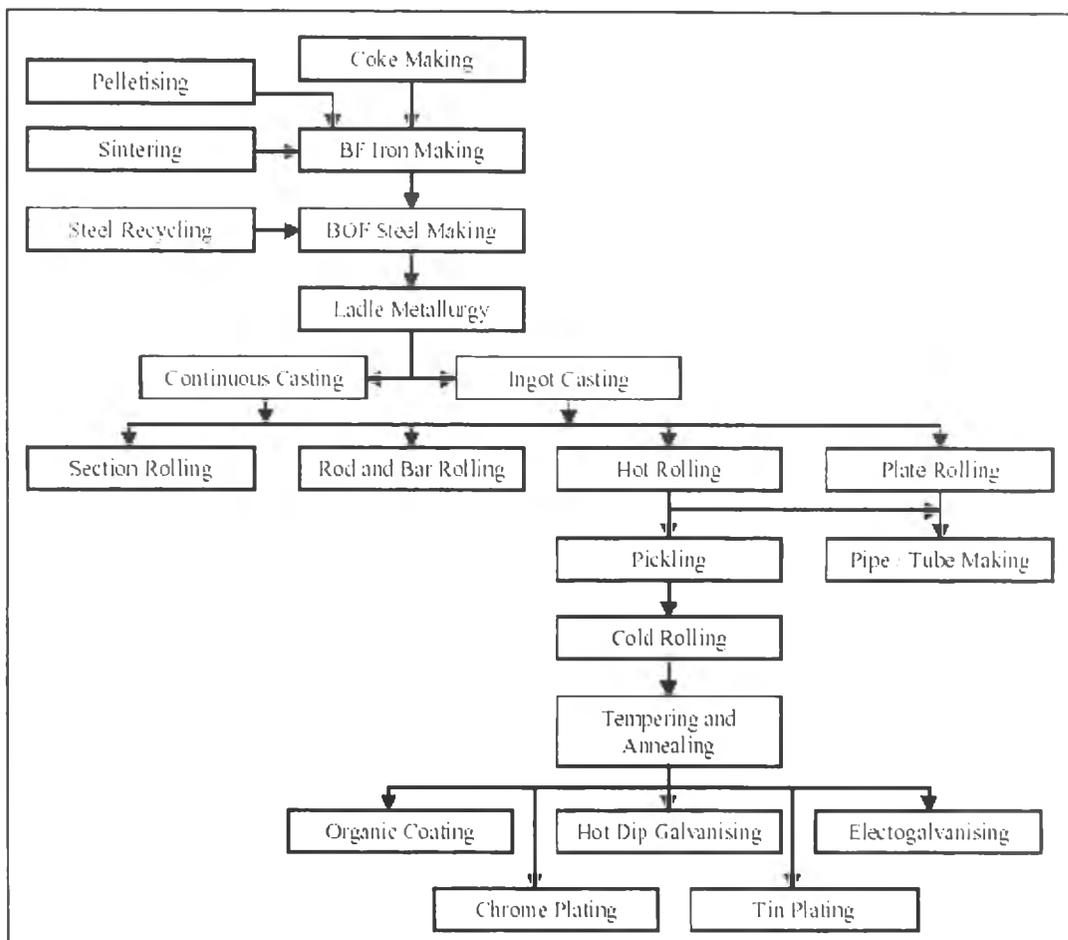
##### 2.1.1 Steel making

Currently, there are two process routes that dominate global steel manufacturing, although variations and combinations of the two exist. These are the 'integrated' and the 'mini-mill' routes. The key difference between the two is the type of iron bearing feedstock they consume. In an integrated works this is predominantly iron ore, with a smaller quantity of steel scrap, while a mini-mill produces steel using mainly steel scrap, or increasingly, other sources of metallic iron such as directly reduced iron. The integrated steelmaker must first make iron and, subsequently, convert this iron to steel. Raw materials for the

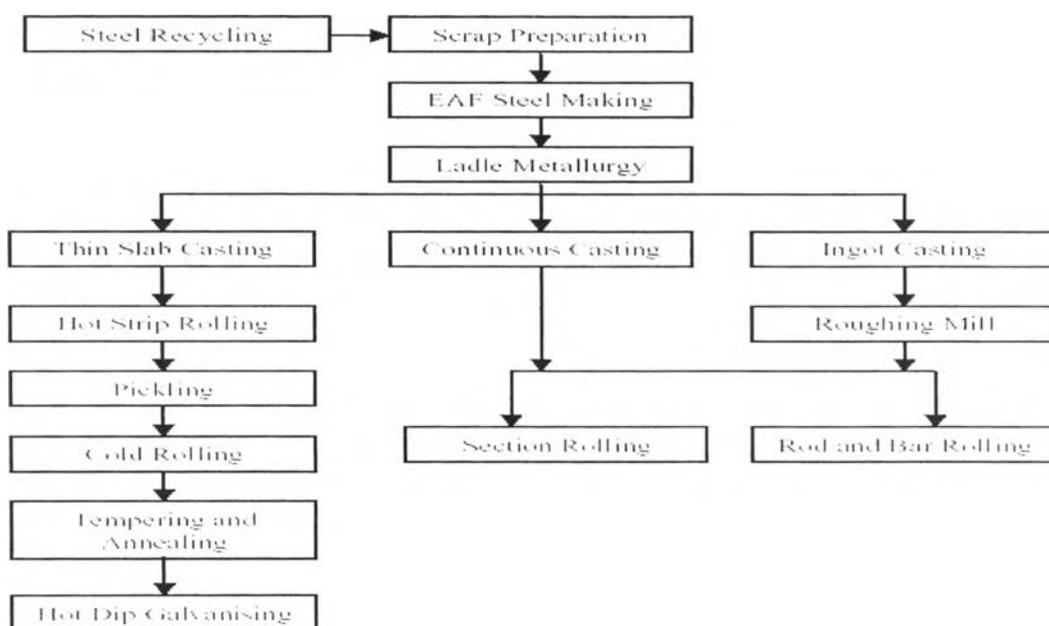
process include iron ore, coal, limestone, steel scrap, energy and a wide range of other materials in variable quantities such as oil, air, chemicals, refractory, alloys, and water. As the process flow sheet in Figure 2-1 shows iron from the blast furnace is converted to steel in the Basic Oxygen Furnace (BOF) and, after casting and solidification, is formed into coil, plate, sections or bars in dedicated rolling mills. The integrated steelmaking route accounts for about 60% of world steel production.

Steel is made in an EAF works by melting recycled scrap in an electric arc furnace (EAF) and adjusting the chemical composition of the metal by adding alloying elements, usually in a lower powered ladle furnace (LF). The process flow sheet shown in Figure 2-2 indicates that the iron making processes, operated on the integrated plant, are not required. Most of the energy for melting comes from electricity, although there is an increasing tendency to replace or supplement electrical energy with oxygen, coal and other fossil fuels injected directly in the EAF. In addition to steel scrap, metallic substitutes such as direct reduced iron (DRI) are becoming increasingly important where scrap availability is limited, where the impurity content of scrap is high or where a localized raw material resource is available. Downstream process stages, such as casting and reheating and rolling, are similar to those found in the integrated route.

A third steel making technology, open furnace steelmaking (OHF), remains in use for about 4% of world crude steel production. Countries where open hearth steelmaking is still employed, based on 200 data, include Russia, Ukraine, Bosnia-Herzegovina, Czech Republic, Poland, Uzbekistan, Latvia, Mainland China, India and Turkey [International Iron and Steel Institute, 2002].



**Figure 2-1:** Process Flow Diagram for Steel Production Using the Blast Furnace Route.



**Figure 2-2:** Process Flow Diagram for Steel Production Using the Electric Arc Furnace Route.

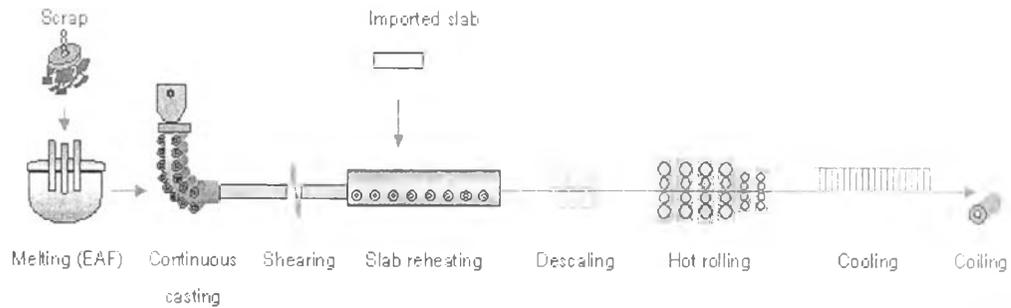
## 2.1.2 Rolling and Finishing

After the molten metal is released from the steel making process, it must be formed into its final shape, and finished to prevent corrosion and also improve properties of the metal. The rolling processes include hot and cold forming.

### 2.1.2.1 Hot Rolling Operation

In Thailand, first step of hot rolling operation is recycled scrap melting in Electric Arc Furnace (EAF) to adjust chemical composition. Then, steel was poured into convenient shapes allied ingots and stored until further shaping was needed it is called slab. Current practices favor continuous casting methods. Some factories, which have no EAF, have to import raw material, slab, from foreign countries. Slab is pre-heated in reheating furnace (Temperature 1100-1250 °C) and is descaled by high pressure water spray and moved to hot rolling where heated steel is passed between two rolls revolving in opposite directions to incremental reduction in thickness (strip). Generally, finishing temperature, strip rolls at last rolling stand, is higher than 870 °C. After that, the strip is cooled by water spray before being moved to coiler (Figure 2-3). The coiling temperature is about 550-710 °C. Final shape and characteristics of a hot-formed piece depend on the rolling temperature, the roll profile, and the cooling process after rolling. The production from hot rolling is called black coil, hot rolled coil or pickled and it is oiled coil as if it passes pickling and removed oil process. Hot rolled coil is normally used in low surface quality which includes construction (Ex. C-channel), pipe (Ex. Pipe and type, spiral pipe), gas cylinder, container, automotive industries (Ex auto part) and used as feedstock for cold rolling mill [Iron and Steel Institute of Thailand, 2002].

Wastes generated from hot rolling include waste treatment plant sludge and scale.



**Figure 2-3: Hot rolling operation process**

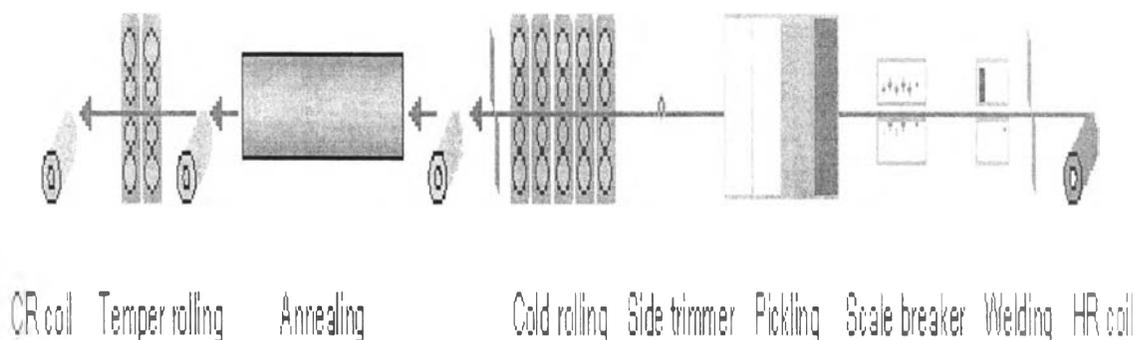
### 2.1.2.2 Cold Rolling Operation

In subsequent cold forming, the cross-sectional area of unheated steel is progressively reduced in thickness as the steel passes through a series of rolling stands. Generally, wires, tubes, sheet and strip steel products are produced by cold rolling operations. Cold forming is used to obtain improved mechanical properties, better machinability, special size accuracy, and the production of thinner gages than hot rolling can accomplish economically.

Hot roll coil is used as a raw material of the cold rolling operation. The first step is to cut and weld the end of each coil to pickling continuously. Then, the hot roll coil passes to a scale breaker to break surface scale and ease acid pickling. After pickling in an acid bath - the coil will be brightening gray sheet, it moves to side trimmer to adjust trim or edge and reduce trim tear effect. After that, reduce thickness with cold rolling process at room temperature. During cold rolling, the steel becomes hard and brittle. To make the steel more ductile, it is heated in an annealing furnace. Process contact water is used as a coolant for rolling mills to keep the surface of the steel clean between roller passes. Cold rolling operations also produce waste treatment plant sludge, primarily due to the lubricants applied during rolling. Grindings from resurfacing of the worn rolls and disposal of

used rolls can be a significant contributor to the plant's waste stream. One of the most important aspects of a finished product is the surface quality. To prevent corrosion, a protective coating may be applied to the steel product. Prior to coating, the surface of the steel must be cleaned so the coating will adhere to the steel. Mill scale, rust, oxides, oil, grease, and soil are chemically removed from the surface of steel using solvent cleaners, pressurized water or air blasting, cleaning with abrasives, alkaline agents or acid pickling. In the pickling process, the steel surface is chemically cleaned of scale, rust, and other materials. Inorganic acids such as hydrochloric or sulfuric acid are most commonly used for pickling. Stainless steels are pickled with hydrochloric, nitric, and hydrofluoric acids. Spent pickle liquor may be a listed hazardous waste.

Utilization of cold roll coil is furnishing, electric appliance, metal fabrication, food can, etc.



**Figure 2-4:** Cold rolling operation process

### 2.1.3 Waste generation and its waste minimization option in hot roll and cold roll mills

#### 2.1.3.1 Hot roll operation

- Emission

The only wastewater normally generated by reheating is the blowdown from cooling towers for furnace component cooling water and minor quantities from leaks and cleanup. This wastewater would

normally discharge to the hot mill scale pit. Air emissions from the reheating furnaces, including soaking pits, are generated by the combustion of the heating fuel. Present day practice in both North America and Japan is to minimize the use of fuel oil and to use coke oven gas or natural gas for soaking pits and to reheat furnaces. Some solid waste is generated from mill scale at the reheating furnaces. It is included in the hot rolling mill solid waste.

The automatic hot scarfing machines used to remove the surface layer and surface imperfections of the hot steel prior to rolling generate fumes, smoke and slag. The fumes and smoke are usually collected in wet-type air pollution control equipment, which generates a wastewater stream. The slag is directed to a slag pit or flume beneath the scarfing machine and is broken up by high pressure (10 atmospheres) water jets and directed to the slag pit or flume. Usually the scarfer wastewater is then directed to the mill scale pit, although in some plants the scarfer has its own scale pit. Since scarfing is an intermittent operation and not all hot steel is machine-scarfed, the wastewater flow is intermittent.

Air emissions result from the generation of iron oxide fumes and other particulate by the hot scarfing process. The solid waste generated by hot scarfing consists of the slag formed by the scarfing action and the particulate recovered by the air pollution control system. In both cases the solid waste is usually flushed into the hot-rolling mill scale pit and is included in the hot-rolling mill solid waste.

Hot-forming wastewater is comprised of direct contact descaling and cooling waters. The most significant sources of wastewater generated by hot rolling are descaling of the hot metal, cooling of hot rolled product, flushing scale flumes under the mill roller tables and the hot scarfer operation and air pollution control. Scale is formed on the surface of the ingots, slabs, blooms, billets and tube rounds when they are reheated for rolling. Some of the scale breaks off

at the furnace exit and during transport on the roller tables. The scale is flushed by water in the flumes under the roller tables to the scale pit.

Scale, oil and grease are the conventional pollutants contained in the hot-forming wastewater. The scale particles range in size from sub-micron to several millimeters. The scale particles are 70-75% iron and consist of ferrous oxide and ferric oxide. With the increase in the proportion of steel processed by continuous casting, the amount of scale produced in hot forming is reduced. The oil and grease found in the hot mill wastewater are a result of oil conditioning, oil spills, line ruptures and excessive dripping of lubricants.

The air emissions from the hot-rolling process consist of fine iron oxide fume generated by the hot rolling and oil fumes from the contact of lubricating oils with the hot steel. In both cases the air emissions are very small and are not quantified.

Solid wastes are generated in the hot-rolling process from the oxide scale that forms on the heated steel and the slag from the hot scarfing operation. In both cases the solid waste is flushed into the scale pit. The majority (coarse fraction) settles in the scale pit and is periodically removed for disposal. This usually contains a significant concentration of oil.

- Waste minimization and pollution prevention in hot rolling operation
  1. The most likely change in hot-rolling technology is the adoption of near net shape, continuous-casting processes, especially for flat products. This technology will enable smaller steel plants to make a wider range of products without the large capital-intensive hot-rolling mills and enable integrated steel plants to continue to produce large tonnage of hot-rolled products with smaller less-capital intensive hot-rolling mills. As mentioned earlier, continuous casting is a pollution prevention technique.

2. The model process developed by EPA for their effluent regulation development for the hot-mill-scale pit effluent includes sedimentation of the raw wastewater in primary scale pits equipped with oil skimmers. Both the oil and the scale removed by this step are reclaimed. Between 60 and 75% of the scale pit effluent is recycled to the process or other mill uses that do not require high quality water. The balance of the scale pit effluent is treated in a roughing clarifier with the clarifier underflow being de-watered in a vacuum filter. The effluent from the roughing clarifier is filtered to remove additional the filter effluent is recycled for mill use. A cooling tower is used to reduce the recycling water temperature. Mill scale should be recycled as feasible. Oil mill scale presents recycling and using air-oil mist lubrication systems in the rolling mills rather than grease can reduce disposal problems but oil content. Dust and sludge from the pollution control units are to be recycled where feasible.

#### **2.1.3.2 Cold roll operation**

- Emission

• The majority of wastewater for cold rolling is from the rolling oil system blowdown, discarded rolling oils (unless sold to outside contractors for reclamation), leaks and spillage from the rolling oil system and the cleaning agent used to clean the system, usually tetrachloroethylene or similar cleaning solvents. A minor source of oily wastewater is the mist eliminators on the rolling mill exhaust systems. Air emissions are minor.

The most concentrated wastewater in acid pickling is spent pickle liquor, an acid solution whose strength has been depleted through continued pickling. For continuous pickling operations, a side stream is usually discharged to maintain a constant acid strength in the pickling operation. Because spent pickle liquor is highly contaminated and low in volume, contract hauling off-site has been a common disposal method. Plants that do not have contract hauling discharge the

spent liquor into treatment systems for disposal or regenerate the spent acid for reuse.

The major source of wastewater is the rinsing operation following the pickling step. Although the amount of water used and discharged varies according to the product being pickled, the number of rinsing steps and the type of rinsing operation, the rinse water generally constitutes the highest flow and contributes much of the process pollutant load. Rinse water flows can be minimized with cascade, counter current or high pressure/high temperature spray rinse systems. Other sources of wastewater are the fume scrubber water and absorber vent scrubber water.

If the spent pickle liquor is not regenerated, it becomes a waste which must be disposed of. In some cases it is sold as a chemical for municipal sewage treatment.

Alkaline wastewater results from the cleaning of intermediate steel products prior to their entry into other finishing operations (e.g. pickling prior to hot coating or electroplating). The most significant pollutants contributed by the process are suspended solids, oil and grease and relatively low levels of some toxic metals. These pollutants originate in the alkaline cleaning bath, in the rinsing operation that follows the cleaning bath and from the blowdown of the fume scrubber usually associated with the cleaning operation. There are no significant air emissions generated by alkaline cleaning.

The annealing process generates very little pollutants, which include cooling tower blowdown, NO<sub>x</sub> emissions from the combustion process and discarded refractory material.

The major wastewater flows originating from hot coating operations are:-

1. Dilute rinse waters from rinses following chemical treatment or surface passivation steps and from final rinses after coating. These waters contain suspended and dissolved solids, chlorides, sulfates, silicates, oily matter and varying amounts of dissolved metals (iron, zinc, chromium, tin, aluminum, cadmium) depending on which coating metal and process is used.

2. Concentrated intermittent discharges (including fluxes), chemical treatment solutions and regenerate solutions from in-line ions exchange system. These discharges contain higher concentrations of the pollutants noted above.
3. Fume scrubber wastewater produced by the scrubbing of vapors and acid mists from the coating steps.

The coating process generates fumes at relatively low emission levels, however, the emissions often include zinc and zinc oxide fumes.

- Waste minimization and pollution prevention in cold rolling operation
  1. The model process developed for EPA for their effluent regulation development for the cold-rolling wastewater consists of an equalization basin equipped with an oil skimmer, chemical addition steps to break the oil emulsions, a flocculation tank and an air flotation system.
  2. The model treatment process developed by EPA for their effluent regulation development for the acid pickling operation wastewater consists of spent acid neutralization, fume scrubber recycle, cascade rinsing, equalization of all wastewater's.

## **2.1.4 Iron oxide waste in rolling mills**

### **2.1.4.1 Scale**

Mill scale is the product of continuous casting, reheating and hot rolling operations. The waster sprays serve to remove scale and other impurities from the steel surface. The scale is collected in scale settling basins.

Hot rolling operations consist of processes in which hot steel billets, blooms and slabs are transformed in size and shape through a series of forming steps to ultimately produce semi-finished and finished steel products. Water is used for direct contact cooling and de-scaling. Cooling water is used to flush the mill stand work rolls and to prevent surface cracking of the steel rolls due to sudden temperature changes. Descaling sprays are also used to remove oxide scale and impurities from the surface of the material being rolled. Cooling and de-scaling water is normally discharged from the mill into scale pits where the heavier solid particles or scale settle out.

- Composition: Rolling mill scale is relatively coarse, with 85 to 90% of the constituent particle >0.006 inches. The iron content, mostly in oxide form, is about 70% (on an oil and moisture-free basis). The oil content of rolling scale is typically in the range of 0.2 to 2% but oil content as high as 10% has been observed. [U.S department of Energy, 1998].
- Production: In Thailand, there was varied quantity of scale generated from rolling operations. For example, approximately 100,000 tons of rolling mill scale were produced, in 2001
- Current treatment options: Some steel plants, rolling scale is sold to re-melting exporter. In addition, some industries are using mill scale as a raw material, including the cement industry.

#### **2.1.4.2 Sludge**

Rolling sludge is generated during hot rolling and cold rolling operations. After the mill scale is removed from the cooling and descaling water used in the hot rolling operation, the semi-cleaned water is then normally sent on to a treatment plant where the fine particulate (sludge) are removed. Process water is then either recycled back to the mill and/or discharged.

In cold rolling operations, flat steel products are reduced in thickness without preheating. An oil-water solution is applied to dissipate heat from both work rolls and the product as it is mechanically processed and to flush impurities from the surface of the steel. The rolling solution is recovered and recycled within the mill, the periodically discharged to an oil recovery plant. There, the rolling oil is recovered and typically returned to a refiner. The processed solution from the recovery plant is discharged to a treatment plant where the sludge was removed.

- Composition: Rolling sludge consists of oil, grease, water and fine-grained solids. The iron content of rolling mill sludge typically varies from about 30 to 60% iron. Generally rolling sludge is 100% minus 20 mesh, moisture content can range from 20 to 50% and oil

content can range from 1.5 to 30% [U.S department of Energy, 1998].

- Production: In Thailand, approximately 20,000 ton of rolling sludge was produced in 1999.
- Current treatment options: Sludge from hot and cold rolling operations (treatment plants) often are landfilled. In a new technique, sludge will be disposed like some oily waste which is packed in small containers (1 kg) and sent to incinerate in cement kiln in Thailand [GENCO]
- Trends and Drivers: As with mill scale, sludge is bonded to oil-grease that is difficult to remove and impedes the recycling of this by-product residue within the steel plant.

## 2.2 Sludge/ Oily sludge

“A semi fluid mass of sediment resulting from treatment of water, sewage and/or other wastes which contaminated with waste oil.”

In Thailand, the management method of sludge is landfilled in security landfill (GENCO). However, the management could be done in several ways.

Petroleum sludge treatment process (PST) separated petroleum from water-in-oil emulsions and sludges. The process could reduce the amount of waste requiring disposal by 95%, at a fraction of incineration costs. Highly stable emulsified petroleum wastes were heated and fed into a pressurized vessel, where wastes separated into oil, water, and solids. The oil could be recovered and reused. The process occurred in one vessel and requires only a feed pump and a heat exchanger. The PST process was 10 times less expensive than using incineration, and its use could reduce disposal costs by a factor of ten. PST could be used for other oil-in-water emulsion, such as those generated by the food processing industry.

The Malaysian oil industry discharged come 1.5 million tons of liquid sludge annually, with a BOD of about 25,000 ppm. This had a greater polluting effect than the wastes produced by the entire population of the country. J.L.R. Kirkaldy (1982) studied in the production of palm oil the palm fruit, after wet heat treatment, was crushed in a continuous press thereby expelling a roughly equal mixture of palm oil

and 'fruit juice'. The cage of the press was also flushed with hot water to keep the perforations clean, and the combined mixture was passed to a settling tank where most of the palm oil was skimmed off. The lower aqueous sludge was discharged as waste. Approximately one and one quarter tons of sludge was produced per ton of oil, but this varies with the type of press used. Moreover he collected the management. An American-Norwegian company had proposed that the combined product of the press, i.e. the oil and the sludge, be passed to a multiple effect evaporator which strips off the water together with some volatile organic solids. The oil now contains only suspended solids and centrifuging or filtration, after which the oil was stored for sale, removed these. The recovered solids were re-pressed to recover some additional oil. Capital cost of this system was estimated to be M\$2.5 m for a mill producing 100 ton/day of oil. Energy costs were likely to be fairly high but lower than those of the Faculty of Agriculture were since the multiple effect evaporator had a much higher thermal efficiency than the rotary drum drier.

An Australian company had proposed that the sludge be first mixed with the fibrous waste from the press and the mixture screened by special vibrating screens. The filtrate, which was now said to be relatively low in suspended solids and free flowing, was concentrated to syrup in a falling film evaporator. This system would also have a high-energy demand but this is partially offset by the sale of the syrup as an ingredient in animal food. The capital cost is estimated to be around M\$1.6 million for a 100-ton/day oil mill.

A British company with a local subsidiary was investigating the possibility of using high speed fermentation techniques similar to those used in modern breweries, to grow filamentous fungi on the sludge. The fungi were removed and the resultant liquor was then subjected to classical anaerobic and aerobic treatment prior to discharge. The capital cost was relatively high (about M\$3.5 million for a 100-ton/day mill) but the fungal mass-produced had a 45-55 % protein content which makes it a valuable animal food. Energy costs were said to be low. In the Chemical Engineering Department of the University of Malaya, another process was being developed. In this case extracting the sludge with a suitable solvent broke the emulsion. The aqueous phase was then free flowing with a COD of about 10,000-ppm i.e. a reduction of about 80%. The suspended solids could now be easily removed by

filtration or centrifuging, and the filtrate was subjected to standard aerobic treatment. This process offers two saleable products, a low grade palm oil and the filtered solids. Energy costs were comparatively low and the capital cost for a 100-ton/day plant was of the order of M\$1.75 million.

On-Site Green technique (OGT) of UNEP (1997), Category: Waste liquid and sludge; Data no.411) studied in recycling of sludge developed in effluent treatment in Japan. Generally, the iron oxide sludge had disposed in effluent treatment by landfilling. Through a waste disposal company, the company found a company that could buy the sludge. The company introduced equipment for drying and incineration. Incineration causes the sludge to lose organic substances and moisture and to turn into inorganic oxide of which over 65% of it was iron oxide. Thus, the company succeeded in selling the substance as glaze material to a tile maker in Fukui Prefecture.

## **2.3 Microwave extraction**

### **2.3.1 Theoretical considerations**

Microwave-assisted extraction (MAE) utilizes electromagnetic radiation to desorb pollutants from their matrices. The microwave regions considered existing at wavelengths from 0.3 mm to 1 m. and frequencies of 100 GHz to 300 MHz. While the whole of this electromagnetic region is potentially available for use, this is not the case. All microwave ovens (domestic or scientific) operate at 2.45 GHz only.

The essential components of a microwave system are a microwave generator, wave-guide for transmission, resonant cavity and a power supply. At the microwave frequency, electromagnetic energy is conducted from the source to the cavity using a wave-guide (or coaxial cable). The microwave generator is a magnetron. The magnetron is essentially a cylindrical diode, in an axial magnetic field, with a ring of cavities, which acts as the anode structure. It is these cavities which become resonant or excited in a way that makes it a source for the oscillations of microwave energy. These cavity magnetrons were extensively developed from the 1940s in the USA for terrestrial and

satellite communications, i.e. radar and radio astronomy. However, it is the use of microwaves for heating that is important. Historically, Percy Spencer who was working for Raytheon in the USA made the discovery of the magnetron as a heating source in 1946. He noticed that a sweet in his pocket melted when he had been standing close to the magnetron source. He then went on to demonstrate that corn would 'pop' when placed in close proximity to the source. This chance discovery led to the first commercial microwave oven for domestic use appearing in the marketplace in 1967.

The heating effect in microwave cavities is due to dielectric polarization, i.e. the displacement of opposite charges, of which the most important type is dipolar polarization. In this situation, the polarization is achieved by the reorientation of permanent dipoles by the applied electric field. This means that under microwave conditions, a polarized molecule will rotate to align itself with the electric field at a rate of about  $10^9$  times per second.

### 2.3.2 Instrumentation

The high cost differential between microwave ovens for domestic use and for microwave assisted extraction can often preclude the purchase of a dedicated MAE system. However, for safety reasons (explosions in the presence of organic solvents) it is recommended that only dedicated systems be used. Two types of microwave heating systems are available commercially, the operation of which relates to the sample container arrangement. In the first type, the sample is heated in an open glass vessel fitted with either an air or water condenser while the second approach utilizes closed sample vessels constructed in microwave transparent material.

In the open-style system individual sample vessels are heated sequentially. The system operates, much like Soxhlet apparatus, inasmuch as the organic solvent is seen to be refluxing within the condenser.

Another is Closed-vessel; a sample can be contained in pressure vessels or heated at atmospheric pressure.

The stirring device is built-in bottom plate of the cavity of microwave instrument for chemical reactions. Motor -driven powerful magnets rotate below the cavity, generating a rotating magnetic field in the cavity. By placing a magnetic bar in a vessel, a stirring effect could be obtained no matter where the vessel was placed, even if the vessel itself was rotating inside the cavity.

The advantages of stirring in a microwave unit

- Faster reactions via increased surface area contact between sample and reagent
- Accelerated extraction with organic solvents
- Extractions could be conducted at lower temperatures, avoiding potential breakdown of heat-sensitive compounds
- Heating of non-polar (microwave transparent) reagents (N-hexane, toluene, etc.) through the use of Weflon coated stirring bar. No need to add microwave absorbing reagents (e.g. ketones) to the solution
- Improved organic synthesis reactions, saponifications , etc.

John Morris Scientific Co.,Ltd studied the advantages of stirring for extraction. In this report 100 ng./g PCB and 500 ng./g in clay extracted aroclor 1016 and aroclor 1260 with and without stirring. The results showed that without stirring % yield of aroclor with stirring were better value. In 100 ng. /g PCB; aroclor 1016 was 81 %, RSD of 3% for stirring, 75 % for without stirring , RSD of 5% and aroclor 1260 was 73 %, RSD of 4% for stirring, 65 % for without stirring, RSD of 4%. In 500 ng. /g PCB; aroclor 1016 was 84 %, RSD of 2% for stirring, 79 % for without stirring, RSD of 3% and aroclor 1260 was 89 %, RSD of 2% for stirring, 87 % for without sirring, RSD of 3%

### 2.3.3 Methods of analysis : Extraction from solids

The use of a microwave oven for sample preparation was first done in 1975. In this case the microwave oven was used to destroy the organic matter, using combinations of nitric acid with perchloric acid or hydrogen peroxide, of certified reference samples prior to elemental analysis. So while this was the first application of a microwave oven for wet ashing, the first application of a microwave oven for the microwave-assisted extraction of analytes from matrices using organic solvents did not appear until 1986. In this work, the microwave oven was used to extract analytes from soil, seeds, foods and feeds using methanol or methanol-water for polar compounds and hexane for non-polar compounds. The microwave oven was operated in short 30s duration and after cooling repeated several times. This approach was compared with the traditional approaches of Soxhlet and shade-flask extraction. In every case, the recoveries obtained by microwave-assisted extraction were comparable with those obtained using the traditional approach. While this paper is of historical importance, its use of a domestic, household microwave oven with organic solvents is not recommended because of fire risk. Modern commercial systems for microwave-assisted extraction have safety features which minimize the risks involved in heating organic solvents.

Onuska and Tery slurry spiked air-dried sediment with a range of organochlorine pesticides and then left the samples to age for at least one month prior to MAE extraction. This paper reported the first results from Environment Canada who have patented the process, using the terminology, Microwave extraction Process (MAOTM). The results highlighted the dependence on organic extraction solvent; iso-octane:acetonitrile 1:1 being preferred to the individual solvents; sediment sample moisture, a minimum water content is necessary to perform MAE with the best results obtained with 15 % water level; and, extraction time, at least 3 min required. The results, based on  $n=5$ , of the extraction of 15 OCPs from a sediment sample spiked in the range 50-250  $\mu\text{g}/\text{kg}$  were good, the minimum recovery was 74 %

with and RSD of 3% for p,p'-DE and the best recovery was 95.3% for methoxychlor with an RSD of 3.9%

The recovery of 20 OCPs from spiked soils using MAE was reported by Lopez-Avila et al. Using the following MAE conditions: temperature, 115 °C; extraction time, 10 min. at 100% power; and 30 ml of a 1:1 acetone : hexane solvent mixture, the recoveries of the OCPs spiked at the 50 ng g<sup>-1</sup> level were assessed from clay soil, topsoil, sand, organic compost and topsoil with 5% humic acid. The results showed that the sand matrix produced the cleanest extracts, the highest recoveries (mean recovery of the 20 OCPs was 83.4 % with an RSD of 10.6 %) and the best precision (typically 2-3 %, based on three determinations). Recoveries from the other matrices were only slightly different (clay soil, mean recovery 88.8 % with an RSD of 30.0 %, n=16) with poorer recoveries being obtained from the top soil with 5% humic acid added (mean recovery 71.9 % with an RSD of 24.9 %, n=20) and the topsoil only (mean recovery 72.9 % with an RSD of 20.4 % , n=20). The poorer precision in all cases should be noted.

V. Lopez-Avila and team (1995) studied 16 phenolic compounds were MAE from clay soil, topsoil, sand, organic compost and topsoil with 5% humic acid using the following conditions: temperature, 115 °C; extraction time, 10 min at 100 % power; and 30 ml of a 1:1 Acetone:N-Hexane solvent mixture. The recoveries of the phenolic compounds, spiked at the 50 ug g<sup>-1</sup> level, were assessed. The results indicated that 70% of the total samples analyzed gave recoveries above 70%. In addition, 2,4-dinitrophenol and 4-,6-dinitro-2 methylphenol appear to have degraded or are irreversibly adsorbed; no such effect was noted for the extraction from sand. The precision of the data, in most cases, is excellent with RSD values of < 10% in 93% of samples extracted and analyzed.

A chemometric approach, based on a central composite design, had been applied for the MAE of phenol and methylphenol isomers from spiked soils that have been aged for 25 days. The variables considered and their limits were as follows: temperature, 70-130 °C; proportion of acetone, 20-80 %; and solvent volume, 15-50 ml, at a fixed extraction time of 10 min and for 5 g of sample. Temperature was found to be significant for all four phenols studied while the proportion of acetone to hexane and the solvent volume were found to be significant in some cases. It was concluded that 10 ml of acetone:hexane (80-20) at 130 °C was the most appropriate, producing good recoveries.

In the MAE method of EPA111 recommended extraction conditions at temperature : 100-115 °C, pressure : 50-150 psi, time at temperature : 10-20 min, cooling : to room temperature, filtering/rinsing : with sample solvent system. However, EPA method recommended that optimize the conditions, as needed, according to the manufacturer's instructions.

In application note of Milestone, a famous brand of microwave extraction instrument had some recommended conditions for microwave extraction.

- Total TPHs from soil (App. Note #PE-004-SEL) – sample amount was up to 5.0 g., 30 ml of acetone/n-hexane was being reagent, temperature program was at 150 °C, 30 min for extraction and up pressure to 1000 W. (Stirring speed 100%/ Teflon stir bars.)
- Total fat from soybean flour (App. Note #FO-001-SEL) - sample amount 0.2-1.0 g., 15 ml of n-hexane was being reagent, temperature program was at 90 °C, 20 min for extraction and up pressure to 1000 W. (Stirring speed 100%/ Teflon stir bars.)
- Fatty acid from various foodstuff (App. Note # FO-002-SEL) - sample amount 1.0 g., 20 ml of Diethylether was being reagent,

temperature program was at 35 °C, 20 min for extraction and up pressure to 1000 W. (Stirring speed 100%/ Teflon stir bars.)

- Total oil from palm fiber (App. Note # FO-003-SEL) - sample amount 3.0 g., 40 ml of n-hexane was being reagent, temperature program was at 90 °C, 20 min for extraction and up pressure to 1000 W. (Stirring speed 100%/ Weflon stir bars.)
- Total fat from soya seeds (App. Note # RO-004-SEL) - sample amount 0.5-2.0 g., 30 ml of petroleum ether was being reagent, temperature program was at 120 °C, 30 min for extraction and up pressure to 1000 W.(Stirring speed 100%/ Weflon stir bars.)
- Total fat from rape seeds (App. Note #FO-005-SEL) - sample amount 0.5-2.0 g., 30 ml of petroleum ether was being reagent, temperature program was at 120 °C, 30 min for extraction and up pressure to 1000 W.(Stirring speed 100%/ Weflon stir bars.)
- Etc.

#### **2.3.4 Comparison of extraction method**

Generally, the requirements of any extraction technique are that it can produce valid data, rapidly, with minimum operator involvement, be cost effective and satisfy safety considerations for both the operator, other personnel and its location within the operating environment. Table 2-1 compares the merits of liquid-solid extraction techniques [John R. Dean].

**Table 2-1: Comparison of Liquid-Solid Extraction Techniques\*\***

<b>Item</b>	<b>Soxhlet</b>	<b>Sonication</b>	<b>Supercritical Fluid Extraction (SFE)</b>	<b>Accelerated Solvent Extraction (ASE)</b>	<b>Microwave-Assisted Extraction (MAE)</b>
<b>Description of System</b>	Utilizes cooled condensed solvents to pass over the sample contained in an extraction thimble to extract the analytes. Uses specialized glassware and heating apparatus.	Sample is covered with organic solvent, then a sonic horn is placed inside the beaker with the solvent and sample.	SFE uses supercritical CO <sub>2</sub> with and without an organic modifier to extract analytes; pressures of up to 680 atm and temperatures up to 150 °C are used. Collection is either into a liquid solvent or onto a solid phase trap. The latter requires desorption with an organic solvent rinse.	Sample is extracted under high pressure (200 psi) and temperature (100 °C). Solvent and analytes are flushed from the extraction vessel using a small volume of fresh solvent and a N <sub>2</sub> purge. Fully automated.	Microwaves used to heat a sample at either atmospheric pressure and near room temperature (open system) or at elevated pressures (<200 psi) and high temperatures (> boiling point of the solvent (closed system))

**Table 2-1: Comparison of Liquid-Solid Extraction Techniques\*\* (cont')**

<b>Item</b>	<b>Soxhlet</b>	<b>Sonication</b>	<b>Supercritical Fluid Extraction (SFE)</b>	<b>Accelerated Solvent Extraction (ASE)</b>	<b>Microwave-Assisted Extraction (MAE)</b>
<b>Acceptability</b>	Used as the benchmark extraction technique by which others are judged	Considered to be less reliable than soxhlet	Considered to be difficult to develop reliable methods	Later on the market than microwaves	Not been commercially available for organic extraction until the 1990s
<b>Extraction time</b>	4-24 hours commonly used	Initiated for periods of 3-15 min. Typically three time periods might be used	Relatively short extraction times (30-60 min.)	Rapid extraction times (15 min.)	Rapid extraction times (approximates to 5 min. per sample vessel-up to 12 sample vessels can be used i.e. 1 hour)
<b>Solvent usage</b>	250-500 ml per extraction	150-300 ml per extraction	Minimal solvent usage (10-30 ml)	Minimal solvent usage (15-25 ml)	Moderate solvent usage (40 ml)
<b>Cost</b>	Very inexpensive	Relatively inexpensive	High cost	High cost	Moderate cost
<b>Ease of operation</b>	Easy to use	Relatively easy to use but labor intensive	Considered to be difficult to operate	Easy to use	Easy to use because of acceptance of domestic ovens
<b>Sample size</b>	> 10 g	Up to 5 g	> 1 g	> 10 g possible	Up to 5 g

**Table 2-1: Comparison of Liquid-Solid Extraction techniques\*\* (con't)**

<b>Item</b>	<b>Soxhlet</b>	<b>Sonication</b>	<b>Supercritical Fluid Extraction (SFE)</b>	<b>Accelerated Solvent Extraction (ASE)</b>	<b>Microwave-Assisted Extraction (MAE)</b>
<b>Sequential or simultaneous</b>	Individual units required for multiple sample extraction	Sequential operation	Simultaneous or sequential systems available	Simultaneous operation of up to 24 samples	Simultaneous operation of up to 12 samples
<b>Approval of method</b>	EPA	EPA	EPA	EPA	EPA++
<b>Main disadvantage</b>	Large solvent usage	Not automatable; labor intensive	Matrix effects identified; high capital cost	High capital cost; new technique	Require polar solvent; filtration of sample required after cooling
<b>Some suppliers of equipment</b>	-	-	Isco, HP, Diones, Suprex, JASCO	CEM, Prolabo, Milestone	Dionex

++ at the present, it has been a EPA method already (EPA no. 3546)

Microwave-assisted extraction had been compared with Soxhlet, sonication and SFE for the extraction of 94 compounds as listed in USEPA method 8250. Freshly spiked soil samples and two standard reference materials were extracted using MAE (condition: sample, 10 g; 30 ml of Hexane : Acetone, 1:1; temperature 115 °C; and an extraction time of 10 min), Soxhlet extraction (conditions: sample, 10 g; 300 ml of hexane : acetone, 1:1, and an extraction time of 18 hr); sonication (conditions: sample, 30 g; 100 ml of methylene chloride : acetone, 1 : 1 repeated three times; and an extraction time of 3 min); and SFE (conditions: sample, 5 g; 10 % methanol-modified supercritical CO<sub>2</sub> ; pressure, 450 atm; temperature, 10 °C/ and an extraction time of 60 min). For the results reported for the 94 compounds, 51 compounds gave MAE recoveries of > 80% ; 33, 50-79% ; 8, 20-49% and 2, < 19 %. Soxhlet extraction gave similar results: 50 recoveries were > 80 %, 32, 50-79 % ; 8, 20-49 % ; and 4, < 19 %. Sonication recoveries were slightly higher: 63 values were > 80 %; 25, 50-79 % ; 4, 20-49 % ; and 2, < 19%. SFE recoveries were the lowest: 37 values were > 80 % ; 37, 50-79 % ; 12, 20-49 % ; and 8, < 19 %. The best precision was obtained using MAE; RSDs ≤ 90 out of 94 compounds studied. Soxhlet extraction gave the worst precision: only 52 out of 94 samples gave RSD ≤ 10 %.

Dean et al. had compared MAE with Soxhlet and SFE for the extraction of PAHs from contaminated soil. The authors reported that MAE with a polar organic solvent, i.e. acetone, gave excellent recoveries (total recovery of 16 individual PAHs, 422.9 mg.kg<sup>-1</sup>) whereas MAE with a less polar solvent, i.e. DCM gave poorer recoveries (total recovery of 16 individual PAHs, 279.8 mg.kg<sup>-1</sup>). This lower recovery was in agreement with the recovery obtained after a 6-hour Soxhlet extraction using DCM (total recovery of 16 individual PAHs, 297.4 mg.kg<sup>-1</sup>). The highest recovery compared favorably with the results obtained using supercritical CO<sub>2</sub> with 20% methanol (total recovery of 16 individual PAHs, 458.0 mg.kg<sup>-1</sup>). The use of a polar solvent was recommended for MAE at a temperature of 120 °C and an extraction time of 20 min.

Organochlorine pesticides which including Aldrin, α-BHC, δ-BHC, 4,4'-DDT, Dieldrin, Endosulfan I, Endosulfan II, Endrin, Heptachlor, Heptachlor epoxide, Hexachlorobenzene and Hexachlorocyclopentadiene, spiked on soil at the 50

ugkg-1 level for the sonication and Soxhlet extractions and 20 ugkg-1 for MAE (except hexachlorobenzene and hexachlorocyclopentadiene which were spiked at 200 and 100 ugkg-1, respectively), were compared with MAE. The results shown that indicated that the highest recoveries were obtained by MAE 10 in 12 cases.

V. Lopez-Avila and team (1995) studied that six phenols were extracted from an ERA soil (lot no.330) by MAE, Soxhlet and sonication. Both Soxhlet and sonication were done in accordance with EPA methods, 3540 and 3550, respectively. The highest recoveries were obtained by MAE (71 %) compared to Soxhlet (52 %) and sonication (57 %). The precision of MAE was also far superior to both other extraction techniques.

The extraction of six phthalate esters from marine sediment was evaluated by comparing an optimized MAE approach with sonication and Soxhlet extraction. The MAE was performed according to the following conditions: 30 of 1:1 solvent mixture (Hexane : Acetone), at a temperature of 115 °C for 10 min. Soxhlet was done using 300 ml of DCM and extracting for 16 hr. while sonication was done using 50 ml of DCM subjected to sonication in an ultrasonic bath for 15 min. and repeated a further two times. Using spiked marine sediment the mean recoveries of the phthalate esters were 7.9 – 91.0 %, 65.5-89.5 % and 64.6-88.6 % for MAE, Soxhlet and sonication, respectively. The precision of MAE was also better, ranging from 2.9-6.8 %, as compared to 4.9-8.0 % for soxhlet and 7.4-10.17 % for sonication, based on three determinations.

### **2.3.5 Waste recycling using microwaves**

Carnegie Mellon Research Institute (CMRI) 's pioneering research in the use of microwaves to process industrial waste is moving into a new direction-the conversion of waste materials and petrochemicals.

The Applied Advanced Technologies group (AAT) had designed and built a microwave chip washer that was being used to clean scrap metal chips. The process used microwaves to separate waste materials into recyclable and non-toxic materials. A pilot unit is currently being field testes. After treatment in the chip

washer, the clean metal chips and oil were recovered and recycled. The processing solution is treated and reused. The commercial chip washer will treat one million pounds of metal per month. Other waste extraction processes produced additional residual wastes or were not as energy-efficient. The microwave system works at low temperatures, at atmospheric pressures and is a near-zero waste process.

In 1991, AAT and EPRI Center for Materials Production at CMRI began work on using microwaves to break down steel mill sludge into reusable materials to help steel manufacturers avoid costly landfill disposal.

EPRI 1994, Microwave separation of oil-water sludges I: Application to industrial waste sludges : CMP Report No.94-3 determined the applicability and the cost of microwave processing in 24 different types of waste samples obtained from materials production and fabricating firms. Since the project focused on de-oiling wastes containing more than 5 % solids, the samples were further screened in order to select six representative samples for in-depth microwave processing. These samples were treated with a combination of microwaves and chemical release agents. Separation time and quality were monitored. The results showed that waste samples obtained from aircraft maintenance, machine tool, and steel production operations were excellent treatment results. After processing, the solids were free of residual oils. Likewise, recovered oils showed minimal water or solids. Both the cleaned solids and the recovered oil were in a form suitable for direct recycling. It was projected that operating and disposal costs for the commercial microwave processing would be in the range of \$9 to \$15/ton, compared to a sample average of \$153/ton for current waste disposal methods

Next step of the EPRI's study was in 1995, Microwave separation of oil-water II: Application to polymer-treated sludges: Evaluation a microwave-assisted process to de-oil steel mill wastewater treatment plant sludges containing polymers and additives. This report focused on the evaluation the microwaves to facilitate the cleaning of fine metal/metal oxide particles contaminated with oily emulsions. CMRI conducted laboratory microwave studied on twelve representative mill sludge samples provided by American Iron and Steel Institute (AISI) companies. The sludge samples were treated with microwaves and release agents to separate the oil from the solids.

Samples were obtained from hot strip mills, cold rolling mills, and mixed wastewater terminal treatment plants which handled several processes including pickling and oil recovery. Stockpiled sludges were evaluated as well as samples which had been treated with additives for thickening the sludges and clarifying the wastewater. A single stage microwave treatment process was developed. This method, which used single process chemistry, de-oiled ten of twelve sludge solids to a level of less than the target value of 1 % residual oil and grease. The other two sludges retained 1-2% residual oil and grease. The best results were obtained for samples that had been magnetically concentrated to remove excess water and for those that contained a minimum of polymers and other were treatment additives. The CMRI analytical results for % oil and grease were comparable to independent testing.

Both the cleaned solids and the recovered oil were in a form suitable for direct recycling. It was projected that operating and disposal costs for the commercial microwave processing would be approximately \$20/ton, compare to approximately \$50/ton for current waste disposal methods. The microwave-processing unit requires less space than conventional treatment facilities.

EPRI (1996) studied in Microwave separation of oil-water sludges III: Recyclability of process fluid: Laboratory evaluation of the recyclability of process fluid utilized in the Microwave separation of hot strip mill wastewater treatment plant sludges. The project studied on ten consecutive batches of HSM sludge utilizing the same process fluid for the entire trial (with minimal makeup fluid). The separated metallic solids that resulted from the process were evaluated after each trial to verify that the samples met the cleanliness standard of residual oils less than 1% (as defined by the AISI Recycling Task Force Committed). The process fluid and resulting oil were also evaluated for cleanliness after each trial. The consecutive treatment showed consistent and efficient cleaning results with no degradation of the metal solids' cleanliness with residual oils. The metal solids were typically below the cleanliness standards specified by the AISI Recycling Task Force Committee for all ten batches. The process fluid was continually cleaned and reused throughout the batches. Thus, it was concluded that the process fluid should be suitable for continuous use.

The sludge-recycling unit is scheduled to be field tested in early 1998. After successful testing, it is slated to go into commercial production by Thermal

Wave International and Chester Engineering. In addition, AAT had received funding from Governors Technologies Corp. for a two year, three-million-dollar program to develop the conversion of waste or low-grade petroleum into a highly marketable petroleum resource. CMRI had been designated the company's R&D arm for applied development of microwave technology.