OPTIMAL DISPOSAL OF METAL WORKING INDUSTRIAL
WASTE WATER/OIL MIXTURES

Štefanija Klarić, Katica Šimunović, Zvonimir Kolumbić, Ivan Samardžić

Metalworking industry, waste water/oil mixtures, treatment methods

1. Introduction

The metal working industries generate different kinds of wastewaters as a result of processing metal parts/products, and machinery, as well as result of associated activities [1, 2]. The performing operations can be described by two types of activities: (a) manufacturing, and (b) rebuilding/maintenance. The unit operations can be classified in one of following types:

- Metal shaping – casting, deformation, machining, grinding
- Surface preparation/finishing – heat treatment, alkaline cleaning, acid treatment
- Metal and organic deposition – electroplating, vapor deposition, painting
- Assembly operations – lubricating, testing (leak)

Metal working unit operations generate waste waters with very different chemical composition. This paper is devoted to the waste water/oil mixtures. From water technology standpoint it is to differentiate following types of metal working industrial waste water/oil mixtures:

1) Water/oil emulsions – colloidal solutions with dispersed droplets (dimensions from 1 nm up to 1 µm) that can not be separated spontaneously. Water/oil emulsions are stable because of electrical double layers formed around oil droplets.
2) Water/oil suspensions – mixtures with very small uniformly dispersed droplets (dimensions greater than 1 µm) that can be agglomerated and separated spontaneously, but the separation process is long-lasting.
3) Water/oil coarse mixtures – the separation process of drops and larger parts of mixed fluids will be spontaneous and rapid.

In the metal working industry, the quantity ratio of waste water/oil mixtures is very various, ranging from trace of oil in water to trace of water in oil. In the case of inappropriate discharge, such mixtures can cause severe and durable contamination of soils and/or waters.

<table>
<thead>
<tr>
<th>Table 1 Selected properties of pure water and industrial oils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Density, ( \rho ) ( g/dm^3 )</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Dynamic viscosity, ( \eta ) ( (mPa\cdot s) )</td>
</tr>
<tr>
<td>Freezing point, ( t_f/\circ C )</td>
</tr>
<tr>
<td>Boiling point (1.013 bar), ( t_B/\circ C )</td>
</tr>
<tr>
<td>Specific heat, ( J/(g\cdot K) )</td>
</tr>
<tr>
<td>Thermal conductivity, ( A/(W\cdot m^{-1}\cdot K^{-1}) )</td>
</tr>
<tr>
<td>Hydrogen ion concentration, pH/-</td>
</tr>
<tr>
<td>Friction coefficient, steel – cast iron (0.4 for dry friction)</td>
</tr>
</tbody>
</table>

* Pour point, ** Flash point, *** INA Termanol 32
Disposal methods of metal working industrial waste water/oil mixture have to be very carefully analysed. Rough separations of oil and water from mixtures can be relative slowly achieved in settling tanks [5] and primary clarifiers [6] or can be improved and/or accelerated by using appropriate equipments. The separated water can be: (a) evaporated, (b) discharged through the municipal sewerage networks or (c) discharged directly to a nearby recipient. The separated oil can be: (a) used as lubricant/fuel, (b) handled by specialized organization or (c) directly sent back to the producer.

The metal working industry boards make decision about optimal waste water/oil mixture disposal methods on the base of the detailed techno-economical analyses, respecting the global and local ecological norms, regulations and legislation. In such techno-economical analysis it is appropriate to consider the metal working industry as well as all its components as the particular cases of generalised mass/heat exchanger, keeping in mind all significant input and output streams. The block diagrams (Figure 1) are the most suitable form for the system/components brief and clear descriptions. All significant blocks and their input/output streams are being marked by suitable designation. The used designations have to be different and associative. [7, 8]

![Figure 1 Block diagram of the generalised mass/heat exchanger](image)

2. Water and oils in metal working industry

Metal working industries use more or less quantities of following waters:
- Potable water from municipal potable water supply network
- Collected rain water
- Underground water pumped from their own underground water wells
- Water from nearby river or lake

Composition of these waters can be very different and for certain uses they have to be appropriately treated by sometimes costly chemical (lime softening), physical (settling, filtering, degassing), or physicochemical (ion exchange, reverse osmosis, ultra filtration) methods.

The sources of waste waters in metal working industry are:
- Metal working emulsion
- Parts cleaning system
- Electroplating and anodizing system
- Water curtain spray booth
- Paint stripping system
- Floor, equipment, vehicles washing
- Cooling system and boiler blow-down
- Canteen and sanitary objects

All this waste waters have to be appropriately treated before discharging.

The main kinds of lubricating/special oils used in metal working industries are:
- Hydraulic oils, for use in various hydraulic systems
- Circulating oils, for lubrication of low clearance high-speed bearings and spindles, as well as enclosed gears under moderate loads
- Industrial gear oils, for lubrication of heavy duty industrial gears
- Compressor oils, for lubrication of rotary sliding vane and screw air compressors
Metal working oils for lubrication of tool/work-piece contacting surfaces during machining

Metal working water/oil emulsion for lubrication and cooling of tools and work-pieces during machining

Heat treatment oil for quenching

Heat transfer oils, for closed fluid heat transfer systems operating at elevated temperatures

Gasoline and diesel engine oils, for lubrication of gasoline and diesel engines

All these oils consist from mineral base and appropriate pack of additives. During exploitation oil bases were degraded, additives were spent and the oil was contaminated with impurities and/or water. After needed properties were lost or declared time limits were reached, used oils have to be exchanged with new one.

Metal working emulsions are used to cool and lubricate the machining tools and working pieces in the cutting zone during machining operations and help remove chips and swarms (accumulations of the metal and abrasive particles) from the cutting zone. Metalworking fluids also provide corrosion protection for the machined parts and machining tools during pauses. As well as oils, after needed properties were lost or declared time limits were reached, used metal working emulsions have to be exchanged with new one. [9]

Three basic legislative acts which determinate waste management in Croatia are:
1) Zakon o otpadu (Law about Wastes), Narodne novine, year 2003, number 151.
2) Pravilnik o vrstama otpada (Rules about Waste), Narodne novine, year 1996, number 27.
3) Uredba o uvjetima za postupanje s opasnim otpadom (Hazardous Waste Management Regulation), Narodne novine, year 1998, number 98.

3. Methods of waste water/oil mixtures treatment

Gravity separators are used to remove oils and solids from waste water/oil mixtures of metal working industry (Figure 2). Since the densities of oils are less than that of water, they will float and the solids, with greater densities, will sink.

Solids settle out and form the sludge on the bottom of the chamber. As the wastewater flows over the first baffle to separation chamber oil droplets rise to the surface and are trapped behind a second baffle. Consequently, solid can be collected from the bottom of inlet chamber and oil accumulated at the water's surface in the separation chamber can be skimmed off to a tank.

Coalescers (Figure 3) are essentially enhanced gravity separators and they are needed to achieve greater separation efficiency.

Coalescers (coalesce – bind together) with inclined plates provide only a short vertical distance (5 mm) for the small droplets to travel before they encounter a fixed surface. Here they can coalesce with other droplets and continue to rise along the plates to the water's surface. Another coalescing method uses a filter made of fine oleophillic fibers such as polypropylene.
In fact, according to Stoke's law, an oil droplet \( \phi = 100 \, \mu\text{m} \) will rise, approximately 15 mm/min and an oil droplet \( \phi = 20 \, \mu\text{m} \) diameter will take almost 15 minutes to rise the same distance [7]. Coalescing the smaller oil droplets makes them larger and more buoyant, causing them to rise faster. However, the small droplets contained in water/oil emulsion do not coalesce without previous addition of appropriate chemicals (coagulator) for destroying of double layers.

**Skimmers** (Figure 4) can be used to remove free-floating tramp oils (not emulsified) from accessible sumps and settling tanks by oil-attracting wheels, belts or ropes. The skimmers are most effective when placed near a circulating pump, since tramp oil usually drifts to that area.

![Figure 4 Skimmers with wheel and belt](image)

**Centrifuges** (Figure 5) contain a number of coalescing disks that aid in the separation of oil and water from water/oil mixtures. Centrifuges are effective at removing partially emulsified oils also and can remove fine particles if they are greater densities than the water. When a centrifuge is used to remove tramp oil, it needs to be combined with some other unit that removes particles or the centrifuge will clog soon.

![Figure 5 Centrifuge](image)

**Hydrocyclones** (Figure 6) force particles greater densities to the outside while water/oil mixture moves to the bowl’s center. Particles that are forced to the outside congregate and fall to bottom. Some small amount of fluid is carried out with the particulate matter. The forces from the fluid cyclone tend to stabilize fluid emulsions; however, tramp oils may also become emulsified.

**Evaporators** are sometimes for the small-quantity generators of waste water/oil mixtures the most effective and economical disposal method, especially if there are present source of low-cost heat energy. There are two typical cases of evaporation and reuse method: (a) evaporate/condense the water for reuse, and (b) evaporate the water and reuse the oil.

**Filters** are mostly used for removing suspended solids from oil and water/oil emulsion. They uses various types of equipment, the most common of which are cartridge filters, precoat diatomaceous earth filters, sand, and multimedia filters. Most cartridges are disposable; however,
washable and reusable filters are available, which further reduce waste generation. Precoat, sand, and multimedia filters are used mostly for large tanks.

Membrane filters can be used to recycle waste water/oil mixtures [10]. Membrane filtration is a pressure-driven process used to separate solution components based on molecular sizes. Solvent and small solutes can pass through the membrane while the membrane retains and collects larger compounds as a concentrated waste stream. The cleaner permeate can be reused in process.

4. Optimal disposal of waste water/oil mixtures

The optimal waste water/oil mixtures disposal have to be found by system analysis based on costing evaluation and a more or less formalized operation research method.

4.1 Costing evaluation

The components of costs are capital ($T_C$) and annual ($T_A$) costs. The capital costs consist of:

- direct capital costs:
  \[ T_{C,D} = C_{EC} + C_{DC} + C_{IC} \]
  where:
  - $C_{EC}$ purchased equipment cost, including ancillary equipment (including piping, valves, electrical wiring, instrumentation)
  - $C_{DC}$ delivery cost (based on the equipment weight and a shipping distance)
  - $C_{IC}$ installation cost (including labor and site work)

- indirect capital costs
  \[ T_{C,I} = C_{EN} + C_{AL} + C_{CF} + C_{CC} \]
  where:
  - $C_{EN}$ engineering (10 % of $T_{C,D}$)
  - $C_{AL}$ administrative and legal costs (up to 30 % of $T_{C,D}$)
  - $C_{CF}$ contractor’s fee (5 % of $T_{C,D}$)
  - $C_{CC}$ contingency (15 % of $T_{C,D}$)

During design engineers have to be analysed:

- Readiness (ability to start with operating after longer standstill),
- Reliability (lasting operating without damages)
- Flexibility (reliable operating under variable conditions)

Inability to start, unexpected standstill due to the damaging of the equipment, as well as malfunction by overload/underload, can provoke serious pollution of the environment.

The annual costs consist also of:

- direct annual costs:
  \[ T_{A,D} = C_{RM} + C_{OL} + C_{EC} \]
  where:
  - $C_{RM}$ raw material costs (chemicals)
  - $C_{OL}$ operating labor and material costs (for operation of the process equipment)
  - $C_{EC}$ energy costs (based on total energy requirements)

- indirect annual costs:
  \[ T_{A,I} = C_{MC} + C_{TI} + C_{Am} \]
  where:
  - $C_{MC}$ monitoring costs (periodic analysis of wastewater effluent samples to ensure that discharge limitations are being met)
  - $C_{TI}$ taxes (wastes disposal) and insurance
  - $C_{Am}$ amortization (5 ÷10 % of $T_{C,D}$)

Helpful data for costing evaluation can be found on EPA Internet sites (Environmental Protection agency)

4.2 Dynamic programming

An appropriate method of operation research is dynamic programming which was developed for optimisation of systems that can be divided in several stages. The decisions made at each stage contribute to overall systems objective function. [11, 12] Objective functions can be represented as:

\[ F(X) = \min_{x_i} \left\{ \sum_{t=1}^{n} t \cdot x_t \right\} \]
where \( i = 1, 2, \ldots, n \) – designation of the component,

\( x_i \) – part of the recourse \( X \) given to the component \( i \),

\( f \cdot x_i \) – costs which follows distribution \( x_i \).

Constrains are:

\[
\sum_{i=1}^{n} x_i = X \quad \text{and} \quad x_{i,\text{min}} \leq x_i \leq x_{i,\text{max}}
\]

Distribution develops in stages that can be represented as:

\[
f_k(j) = \min_{x_{i,\text{min}} \leq x_i \leq x_{i,\text{max}}} \left\{ t_i \circ x_i + f_{k-1}(j - x_i) \right\}
\]

where \( k \) – designation of the stage,

\( j = 1, 2, \ldots, X \) – part of the recourse \( X \) given to the components.

In the first stage \((k = 1)\), the first component obtains the part of the recourse \( x_1^* \) for that \( f_1(j) \) has the minimal value. The leftover recourse is distributed to the leftover \((n - 1)\) component. The result is:

\[
F(X) = F(x_1^*)
\]

where \( x_i^* \) - optimal part of the recourse \( X \) given to the component \( i \).

5. Conclusion

Inappropriate discharge of the water/oil mixtures of metal working industry can cause severe and durable contamination of soils and/or waters.

The paper set up the base for techno-economical system analysis of the optimal disposal metal working industrial waste water/oil mixtures.

The future effort has to be devoted to the case studies – quantitative data collection about concrete cases meted in Croatia’s metalworking industry gathering as well as their optimal resolutions.

References


