PROCESS INTEGRATION FOR WASTEWATER MINIMIZATION

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ABSTRACT

Process integration methods offer a systematic approach to the design of production facilities. These methodologies can be adapted to focus on pollution prevention objectives. The present paper discusses one such application - the use of numerical optimization to identify "minimum wastewater" or "minimum freshwater" designs for processing systems.

INTRODUCTION

Over recent years a new branch of chemical engineering known as "process integration" has come into being. Under this banner, several different systematic approaches to the design and retrofit of industrial processes have developed. Each of these approaches starts with an overview of the process as a whole, rather than starting with individual unit operations or pieces of equipment. In this way a "correct" structure can be developed for the overall plant, with individual items of equipment being fitted into this structure. The focus of this work has generally been cost minimization, with the emphasis on the trade-off between capital and operating costs. However, it has now been recognized that essentially the same methodologies can be used to explore the three-way capital cost/operating cost/environmental trade-off.

Process integration methodologies can be classified under three major headings:

- Numerical Modeling
- Knowledge-Based Approaches
- Pinch Analysis$^{SM}$

The present paper focuses on a specific application of the numerical approach - namely the minimization of freshwater use or wastewater generation for a production facility. The methodology has been coded in a software package known as "WATERLILY" ($^1$).

PROCESS INTEGRATION METHODS

Numerical Modeling

The numerical modeling approach is based on process simulation using simplified mathematical models of the process. These are often combined with cost equations to quantify the impact of design decisions on process economics. Graphical representations, often called "cost diagrams", are commonly generated to provide a visual representation of the effect of varying design and/or operating parameters ($^2$).

This approach has been applied to certain environmental problems before. For example, it has been used to relate the emissions from an oil refinery to design options and operating conditions ($^3$). This enables engineers to explore the impact of process changes on both cost and emission levels, allowing cost vs. emissions limit curves to be developed. This approach could also potentially be used by regulatory agencies to assess the economic implications of setting different emission limits, and to set "performance standards" accordingly.
Knowledge-Based Approaches

There are a number of process integration methods that fall under the general heading of "knowledge-based approaches", all of which can be applied to pollution prevention problems. These include heuristic approaches (1), the hierarchical review method (6), and artificial intelligence (4). Each of these approaches provides a systematic framework for evaluating a process flow sheet, based on a knowledge of the common features of similar process designs. The result is the rapid development of new design or retrofit concept, often starting with minimal data. In new plant design, use of procedures of this type generally results in one or more "good" (i.e. cost-effective, with low emissions) design(s) for the process; in retrofits, they typically generate a list of potential process improvements for use in revamp projects.

Pinch AnalysisSM

Pinch AnalysisSM (7) is a systematic technique for analyzing heat flows through industrial processes. It is widely used to determine the scope for energy savings in industrial operations and to define possible process changes to reduce intrinsic energy consumption. The trade-off between energy consumption and capital investment can also be assessed at this stage.

In the environmental context, this approach is useful primarily as a means of determining the extent to which energy consumption can be reduced, with the attendant reductions in NOx, SO2, and CO2 (6). However, it also provides some guidance in the generation of design options for the reduction of other, process-related emissions (6, 10). The pinch method has also been adapted for analyzing mass transfer, especially in dilute aqueous systems (11). This offers a new approach to the analysis of wastewater systems, which has been incorporated in a software package called STAR (12).

The three different branches of process integration have somewhat different areas of application, and tend to yield different, complementary results. The numerical modeling approach, for example, is best suited to situations where only a limited number of well-defined design options require evaluation. For complex processes with multiple variants the simulation effort can become overwhelming, and the other approaches - especially knowledge-based methods - are needed to identify potentially attractive options and narrow down the scope of the problem. The pinch approach is good for identifying fundamental insights into heat transfer and mass transfer problems, which can result in step-change design improvements. The case study at the end of this paper illustrates the interaction that is possible between two different process integration methods.

DEFINING THE PROBLEM

Wastewater sources in industrial processes fall into three major categories:

1. Water is introduced into a process deliberately to remove impurities that would otherwise disrupt processing operations (e.g. desalting in oil refining, brownstock washing in Kraft pulp mills, various solvent extraction operations, etc.). This creates a wastewater stream that removes the impurities.

2. The wastewater is an unavoidable byproduct of process operations (e.g. decanted water removed from crude oil or water generated by reaction processes).

3. The wastewater is a byproduct of utility water use (e.g. blowdown from boilers or cooling water systems).

The first type of wastewater generation (i.e. deliberate water addition to remove impurities) is typically characterized by a requirement to remove a fixed amount of one or more contaminant(s) (e.g. salt in a crude oil desalter), and is subject to maximum contaminant concentrations into and out of the unit in which the mass transfer occurs. However, in certain cases there is no fixed quantity of one or more contaminant(s) to be removed. In the desalter, for example, the wastewater (brine) contains some oil - an undesirable but inevitable consequence of contacting oil and water. It is the bulk concentration of
the oil in the wastewater, rather than the absolute quantity, that is typically constant for steady desalter operation.

The second type of wastewater generation (generated by process operations in which water is not added specifically to remove contaminants) typically results in a fixed mass flow of "secondary water", with fixed contaminant concentrations. Neither the flow nor the composition is generally amenable to modification. However, in some cases the "secondary water" can be used in place of freshwater in operations use water (subject to acceptable contaminant levels).

The third type of wastewater generation (blowdown from utilities) is generally associated with the concentration of trace impurities. This arises because make-up water (which always contains some impurities) has to be added to the utility system to replace lost water - e.g. evaporative losses from cooling towers, steam losses (due to leaks and live steam injection) and condensate losses from steam systems. The losses are generally substantially pure water, so in the absence of a blowdown the contaminants from the make-up would concentrate to unacceptable levels within the utility system. Chemicals (e.g. biocides) are also commonly added to water within utility systems, and the blowdown stream inevitably contains some of these materials.

The Pollution Prevention Hierarchy
The "pollution prevention hierarchy" ranks the basic means of reducing emissions in terms of global desirability. Several versions have been proposed, of which the following (showing the ranking, from most to least desirable) is one:

1. Source Reduction
   e.g. use cleaner feed material; eliminate leaks

2. Reuse & Recycle
   e.g. reuse waste from one unit as a feed to another; recycle contaminated material to the unit that generated it, with a small purge to maintain acceptable contaminant levels.

3. Treatment
   e.g. acid neutralization; incineration

4. Safe Disposal
   e.g. landfill

Any pollution prevention option can in principle be classified under one of these categories, although in practice the classifications are not always clear-cut. For example, "treatment" options could be used to make a stream suitable for reuse or recycle (these are commonly known as "regeneration" options); or they could be precursors to safe disposal ("end-of-pipe" treatment).

The present work focuses on reuse and recycle of wastewater, and on regeneration options. The WATERLILY software package has been developed to identify design options that minimize the use of freshwater or the generation of wastewater for any given production facility. The user specifies all units that generate wastewater and all regenerators. The program then analyzes all possible means of interconnecting these units, subject to user-specified constraints, and thus determines either the minimum amount of freshwater make-up or the minimum flow of water to end-of-pipe treatment required for the system to work.

Regeneration
There are many different types of regeneration equipment, such as filters, membrane separators, sour water strippers and ion exchange systems. The objective of all of these is to remove contaminants to make the water stream suitable for reuse.
In almost all regeneration operations (e.g. membrane systems) the incoming contaminated water is split into two streams - one "pure" (i.e. suitable for reuse or recycle), and the other containing the contaminants at increased concentration. Thus only part of the incoming flow can be reused. Moreover, most regenerators do themselves have to be "regenerated" - e.g. filters require periodic back-flushing, and ion exchange resins require restoration to their original ionic content. This "regeneration of the regenerators" typically requires additional use of freshwater, and thus increases both the use of freshwater and the total wastewater flow.

Wastewater Minimization

The principal purpose of the WATERLILY program is to determine the minimum freshwater or wastewater flow that is required to allow the process under consideration to operate. The program evaluates all water users, wastewater generators, secondary water generators and regenerators. Based on this analysis it determines the process structure (i.e. interconnections between units) and internal flow rates that will minimize the water usage or overall discharge rate.

The current version of the program does not incorporate any cost functions, and therefore can not perform explicit monetary optimizations. However, regeneration units are commonly the largest variable component in the costs, and regenerator cost is primarily a function of wastewater loading. For this reason, a feature is provided which allows water flow through the regeneration units to be included in the objective function. The user can specify the weighting to be given to this term. This feature can be useful, for example, if there are multiple feasible solutions with the same freshwater flow but different regenerator loadings. By adding a weighted regenerator loading to the objective function, the optimizer can be driven towards the solution that achieves minimum freshwater use with the minimum flow through regenerators. Note, however, that the optimizer can not simultaneously minimize both freshwater flow and regenerator flow. The additional term in the objective function, and the ability to adjust its weighting, is a user-driven feature intended to help steer the solution in the most desirable direction.

Optimization Philosophy

The wastewater minimization problem is highly non-linear, and is not readily amenable to linear approximations. For this reason, the WATERLILY package uses the GINO non-linear optimizer (14). The mathematics of non-linear optimization do not guarantee a "global optimum". The solution that is found is dependent on the initialization and is in general a "local optimum" - which may or may not also be the "global optimum". In practice it has been found that a global optimum is easy to locate for wastewater problems in which there is no regeneration. In these cases the problem appears to be "convex", and is insensitive to the initialization. Where regeneration is included the problem is more difficult, and multiple initializations may be necessary. However, experience has shown that "realistic" initializations generally lead to the true global optimum. Appropriate initializations may be developed from a knowledge of the physics and chemistry of the process, or by using insights obtained from other process integration methods (notably hierarchical review or mass transfer pinch analysis).

CASE STUDY

The wastewater minimization technique is illustrated by an oil refinery example. The structure of the wastewater system (Figure 1) is loosely based on that of part of Amoco's Yorktown refinery (15). Concentrations assumed for contaminants in the different streams are based on data from various literature sources (11,16).

The wastewater system handles effluent from the desalter, together with sour wash water. There are also additional miscellaneous sour water streams. For convenience these are combined in the present analysis, and they form a "secondary water" stream. A sour water stripper (SWSI) is used to regenerate the sour water. There is also a cooling water system. The highlighted terms are discussed below. Data for this system are summarized in Table 1.
**Desalter and Sour Wash Water**

Desalting is carried out to remove unwanted dissolved and suspended materials from the crude. This process involves contacting water with the incoming oil, and then decanting it. Wash water is used to prevent build up of solids in vapor lines around the refinery - notably in hydrotreating units. Because it is typically in contact with sour gases, the wash water effluent is generally also sour (see discussion on sour water below).

The primary purpose of both the desalter and washing is the removal of definable and relatively small quantities of specific contaminants (mostly salts). However, additional contaminants (notably hydrocarbons and H₂S) are picked up because the desalting water and wash water have to be contacted with liquid and/or vapor streams that contain large quantities of hydrocarbons and H₂S. Small amounts of these contaminants are consequently either dissolved or suspended in the water. This results in a roughly constant concentration of these contaminants in the effluent water, irrespective of water flow. The data in Table 1 reflect the ways the different contaminants behave: Solid contaminants are defined in terms of maximum permissible inlet and outlet concentrations, and a fixed amount of pickup. For the two other contaminants - H₂S and hydrocarbons - maximum permissible inlet concentrations are specified, but the outlet concentration is fixed by equilibrium considerations. There is no pickup specification, because the amount of these contaminants transferred to the water will depend on the inlet concentration and flow rate.

**Sour Water**

Sour water is any water contaminated with H₂S. Its composition may vary considerably, depending on its source. In the present simplified example, it is assumed that all the sour water sources (excluding the sour wash water) are combined into a single "miscellaneous sour water" stream of fixed composition. Sour water is produced in a number of ways, for example:

- Steam ejectors are used to provide the vacuum for the vacuum distillation unit. The condensate obtained from these systems contains hydrocarbons and H₂S.

- Column condensers. Water in column feeds and live steam used for stripping tend to go overhead in distillation columns, and have to be drawn off. These condensates are often contaminated with H₂S.

- Storage tank drains. Water also has to be drawn off tanks in which feed and product materials are held. Depending on the nature of the material being stored this may be contaminated with varying amounts of H₂S, hydrocarbons and dissolved and suspended solids.

**Sour Water Stripper (SWS)**

Sour water stripping is the means most commonly adopted for removing H₂S from refinery sour waters. This is necessary both to recover the H₂S for removal of elemental sulfur and to make the water suitable for reuse or disposal. It is accomplished in a stripping column, using either live steam injection or reboiling. In the present example, the existing plant has a live steam system. The live steam that is injected condenses and mixes with the stripped water. Consequently the water flow leaving the stripper is roughly 30% more than the flow entering. The effluent water is used in the desalter, with excess water going to the cooling system.

**Cooling Water System**

The cooling system differs from the other water users in that it has a water loss of 22.0 te/hr associated with it, due to evaporative cooling in the cooling tower. Cooling towers act as strippers for light components in water. For simplicity in this example, this stripping action is modeled as an equilibrium system for the hydrocarbons and H₂S, with zero outlet concentration for both species. All cooling tower make up contains solids - even if the make up water is notionally "pure". Evaporation from the cooling tower tends to concentrate these, and it is necessary to blow down to prevent build up that would otherwise lead to scaling. Calcium and magnesium compounds, in particular, contribute to this problem. A typical value for the "hardness" of freshwater make up is around 630 ppm.
Blowdown concentrations are typically around five times this value (16). (In the present example, no distinction is made between different solids species, neither is any distinction made between dissolved and suspended solids. For a more rigorous evaluation, additional contaminant species could be incorporated in the data set to account for these.)

Water treatment chemicals, notably biocides, are added to cooling water systems. These generally make the blowdown unsuitable for reuse.

**Base Case Water Usages**

Figure 1 represents the "base case" for this study, both in terms of structure (i.e. equipment items and their interconnections) and water flows. The demand for freshwater is 12.6 te/hr, split between line washing and the cooling system. All of the "miscellaneous sour water" (30 te/hr) is fed to the SWS, together with line washing effluent (7.5 te/hr) - a total regeneration feed rate of 37.5 te/hr. 11.2 te/hr of live steam is used in the SWS, and this condenses and becomes a part of the SWS effluent water stream. The principal use for this "stripped sour water" is the desalter (26.6 te/hr), with the excess (22.1 te/hr) going to the cooling tower. In practice, this excess stripped sour water is problematic, as it contains small amounts of phenols. These create an odor in the vicinity of the cooling tower. It would not be acceptable to discharge this stream outside the refinery, and there is no other potential user for this water within the refinery. A reduction in the volume of the excess would therefore be highly desirable.

In terms of overall water balance, the live steam is additive with the freshwater, so the total "clean water" supplied (as steam or freshwater) is 12.6 + 11.2 = 23.8 te/hr.

**Flow Optimization Without Process Changes**

If the WATERLILY optimization program is run with the data from Table 1, it indicates a "clean water" target (freshwater plus steam) of 23.7 te/hr. This is lower than the usage in the existing design by only 0.1 te/hr, or about 0.4% - a negligible reduction. However, if the objective function for the optimization includes a weighting for the regeneration (i.e. SWS) flow, the target regeneration feed rate in the solution is 30.0 te/hr (down from 37.5 te/hr). At the same time the live steam usage is 9.0 te/hr (down from 11.2 te/hr). These changes represent 20% reductions. As the steam is far more expensive than freshwater make up (typically around $8.00/te vs $0.50/te), this change represents a significant saving - around $132,000/year.

Figure 2 shows the structure identified by the optimizer to achieve the target. The main structural difference relative to the base case (Figure 1) is that "miscellaneous sour water" is used for line washing, rather than freshwater. All the freshwater is added is in the cooling system, and the amount of stripped sour water going to the cooling system is reduced from 22.1 te/hr to 12.3 te/hr. This change represents a significant improvement in the odor problem associated with discharging this water to the cooling tower.

**Flow Optimization With Process Changes**

The published study of the Amoco Yorktown refinery (6) described an analysis of several process units using a hierarchical review procedure. This resulted in a list of several potential means of reducing emissions, including a number of ideas that would reduce stripped sour water flow to the cooling tower. Two of these were:

a. Convert the SWS from live steam to a reboiled system (to reduce the aqueous effluent flow from the SWS).

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1 The structures identified by the optimizer are not necessarily unique - i.e. other structures may be possible that achieve the same target flows for freshwater and regeneration.
b. Replace vacuum steam ejectors with vacuum pumps (to reduce the quantity of sour condensate produced).

These ideas were analyzed using the WATERLILY optimizer. The results are shown in Figure 3 (SWS modification) and Figure 4 (SWS and ejector modifications).

Eliminating the live steam flow in the SWS (Figure 3) means that there is far less excess stripped sour water to send to the cooling system (3.2 te/hr, down from 12.3 te/hr). This should result in another significant improvement in the odor problem. The "clean water" target is 23.5 te/hr - slightly down from the situation in Figure 2 (23.7 te/hr, including water and steam). However, in Figure 3 all of the demand is in the form of freshwater rather than steam. (There is still a need for steam to drive the SWS, but the condensate does not mix with the sour water. Provided the condensate is recovered and returned to boilers the steam does not contribute to freshwater demand.) The flow entering the SWS is still 30 te/hr, as in Figure 2.

The ejectors contribute 5 te/hr to the sour water flow. If they are replaced (Figure 4), the miscellaneous sour water flow goes down from 30 te/hr to 25 te/hr. There is a corresponding reduction in the demand on the SWS, which will reduce steam costs. If this change is made together with the replacement of live steam stripping with a reboiler on the SWS, the flow of stripped sour water to the cooling system is totally eliminated, so there is no longer an odor problem. However, the freshwater demand increases (from 23.5 to 28.2 te/hr). Freshwater is needed not only for the cooling system, but also to supplement the desalter demand. This is simply a water balance issue: eliminating 5 te/hr of sour water creates a need for (approximately) 5 te/hr of water from another source. Of course, there has also been a reduction of approximately 5 te/hr in steam for steam ejection.

Results
The results of the case study are summarized in Table 2. The key benefits that are obtained by optimizing the wastewater system are the reduction of the sour water stripper feed flow (which reduces the operating costs of the sour water stripper), and the elimination of the excess stripped sour water flow (which eliminates the cooling tower odor problem). The operating cost reduction in the sour water stripper is approximately $220,000/year, if all of the identified improvements are implemented. It is difficult to put a monetary value on the environmental improvement in the vicinity of the cooling tower.

CONCLUSIONS
This paper presented an approach to the general wastewater minimization problem based on a numerical optimization technique. The technique was illustrated with a case study based on an oil refinery wastewater system.

The method provides a rigorous solution for the minimum freshwater demand or wastewater generation rate in a production facility, using non-linear programming. The essential elements of the methodology are incorporated in a software package called WATERLILY.

Some pre-screening of process options is desirable before the software is used. This allows the user to identify appropriate regeneration options and process modification opportunities to include in the analysis, and to select some of the most appropriate interconnections between unit operations. This pre-screening can be accomplished with one of the other process integration methodologies, such as hierarchical review or mass transfer pinch analysis.

ACKNOWLEDGEMENTS
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References

1. WATERLILY wastewater minimization software, developed by Linnhoff March, Inc., 9800 Richmond Ave., Suite 440, Houston, TX 77042.


12. STAR pinch analysis software from the Center for Process Integration, University of Manchester Institute of Science and Technology, P. O. Box 88, Manchester M60 1QD, England.


14. GINO non-linear optimization package, from LINDO Systems, Inc., P.O. Box 148231, Chicago, IL 60622.

TABLE 1: DATA SET FOR REFINERY WASTEWATER EXAMPLE

<table>
<thead>
<tr>
<th>Process</th>
<th>Water Loss (te/hr)</th>
<th>Contaminants</th>
<th>max C_in (ppm)</th>
<th>max C_out (ppm)</th>
<th>Pickup (kg/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Line Cleaning</td>
<td></td>
<td>Hydrocarbon</td>
<td>50</td>
<td>120^e</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H2S</td>
<td>5000</td>
<td>12500^e</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>140</td>
<td>200</td>
<td>1.5</td>
</tr>
<tr>
<td>2. Desalter</td>
<td></td>
<td>Hydrocarbon</td>
<td>120</td>
<td>220^e</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H2S</td>
<td>20</td>
<td>45^e</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>200</td>
<td>9500</td>
<td>250</td>
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<tr>
<td>3. Cooling System</td>
<td>22.0</td>
<td>Hydrocarbon</td>
<td>220</td>
<td>0^e</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>H2S</td>
<td>45</td>
<td>0^e</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Salt</td>
<td>2500</td>
<td>3115</td>
<td>13.86^b)</td>
</tr>
</tbody>
</table>

NOTES:

* ^ implies outlet concentration is a fixed (equilibrium) value

Pickup represents solids in freshwater make-up. The software used in this study assumes zero contamination in the freshwater make-up. In reality, there would be 630 ppm of hardness in this water. The pickup of 13.86 kg/hr of solids in the cooling system model represents the quantity of hardness introduced if freshwater is used to replace the 22.0 te/hr evaporative loss.

SECONDARY WATER
The secondary water (sour water) flow is 30 te/hr. It contains 45, 4000 and 135 ppm of hydrocarbon, H2S and salt, respectively. Excess secondary (i.e. any that is not used within the unit operations) will require "end-of-pipe" treatment.

SOUR WATER STRIPPER
The sour water stripper is assumed to remove 0%, 99.9% and 0% of the hydrocarbon, H2S and salt, respectively, with no change in water flow rate.

TABLE 2: REFINERY CASE STUDY RESULTS

<table>
<thead>
<tr>
<th>Case Description</th>
<th>Water Flows: te/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Live Steam</td>
</tr>
<tr>
<td>Base Case</td>
<td>11.2</td>
</tr>
<tr>
<td>Optimized:</td>
<td></td>
</tr>
<tr>
<td>- No Process Changes</td>
<td>9.0</td>
</tr>
<tr>
<td>- Reboiled SWS</td>
<td>0.0</td>
</tr>
<tr>
<td>- Reboiled SWS &amp; No Stm Ejectors</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 1: Refinery Case Study: Initial Configuration
Figure 2: Refinery Case Study: Optimized With No Process Modifications
Figure 3: Refinery Case Study: Optimized With Reboiled SWS
Figure 4: Refinery Case Study: Final Solution - Reboiled SWS and No Steam Ejectors