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Revision Memo

- 12/97** The Spent Caustic Handling section has been revised as an introductory section. Detailed description of Spent Caustic is found in DP XX-C4.
A section in Waste Management Preferred Operating Practices was added.
- 12/02** Greater concentration given to recycle and reuse options including description of waste management hierarchy.
Information on affiliate dewatering practices has been added.
Sections on Source Control, Lagoon Sludge-to-BIOX, Rotary Drum Thickeners, and Tank Waste Minimization added.

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1.0 SCOPE

This introduction to solid and liquid waste management provides background information on waste minimization, recycle, reuse, treatment, and final disposal methods. Equipment and processes are described in general terms in order that an applicable overall treatment scheme may be identified. Detail can be found either in the following Design Practice subsections, EMRE Research and Development reports, or other third party references. Plant waste management procedures are also discussed. These procedures are site specific and dependent on local regulation. All sites should review their operations and take its unique physical plant, personnel, and regulatory issues into consideration before developing a waste management plan.

Waste sources discussed include solids (e.g., gravity belt filter press product) and liquids containing significant concentrations of suspended solids (e.g., filter backwash water with Total Suspended Solids (TSS) >1000 mg/L). Wastewater streams with low concentrations of suspended solids (for example, TSS<1000 mg/L like API separator effluent) are excluded from discussion here and may be found in the Water Pollution Control Design Practices ([DP XIX-A](#)).

Spent caustic is briefly discussed in this section. The guidelines and considerations for spent caustic management are found in [Design Practices Section DP XX-C4](#).

2.0 REFERENCES

2.1 DESIGN PRACTICES

Section XIX	Water Pollution Control
Section XIX-A5	Biological Treatment of Wastewater
Section XIX-A8	Activated Carbon Treatment
Section XX-A2	Gravity sludge Thickeners
Section XX-C1	Biological Treatment
Section XX-C3	Solidification and Stabilization
Section XX-C4	Guidelines and Considerations for Spent Caustic Management

2.2 OTHER REFERENCES

1. Archibald, B.B. and Shah, P.S., Santa Ynez Unit Expansion Project Onshore Facilities: Emulsion and Produced Water Treatment Optimization: Solids Handling and Disposal Study, EE.1E-X.88
2. Becker, P.W. et al, MEFA: Minimum Emissions Facilities Assessment, EE.12E.92 and EE. 123E.92
3. Cancellare, M.C. and Wang, J.S., Evaluation of Cement Kilns for the Reuse/Disposal of Refinery and Petrochemical Wastes, EE.10E.93
4. Feerick, C.P., Wang, J.S., and Gaston, P., Low Cost Waste Reduction - A Case Study at the Port Jerome Refinery, EE.4E.95
5. Guide for Reducing Waste Treatment Costs, EE.48E.85
6. Neff, J.W., Lagoon Sludge-to-Biox Treatability Study, EE.80E.2002
7. Neff, J.W., Faber, J.R., Smith, S.T., and Doleman, A.K., No/Minimal Oil to Sewer Catalog, EE.76E.2002
8. Neff, J.W., Sludge-to-Coker Affiliate Experience Catalog, EE.75E.2002
9. Neff, J.W., Silt Screens and Catch Basin Inserts for Reduction of Sludge Generation, 2002 ECS2 524
10. Schinner, C.M., Refining Sludge Reuse in CO Boilers, EE.32E.93
11. Schmehr, D.D., Methods for Prevention and Control of Soil Erosion, EE.91E.89
12. Shah, P.S. and Cancellare, M.C., BRRF Waste Management and MRU Screening Study, 96 GCD 050
13. Tank Maintenance Guide, EETD 0050
14. Wang, J.S., Guidelines for Evaluating Thermal Reuse Options For Disposal Of Plant Wastes, EE.67E.89
15. Wang, J.S., Use of Dryers (Thermal Desorption Technology) for Treatment of Plant Hazardous Wastes, EE.67E.91
16. Wang, J.S. and Hafker, W.R., Waste Management Preferred Operation Practices (POPs), EE.82E.97

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3.0 DEFINITIONS

COD - Chemical Oxygen Demand (COD) is a measure of the amount of chemically oxidizable material in a given sample. It is generally greater than the BOD, the amount of biologically oxidizable material present in the sample. The COD test is simpler and faster than the BOD test. COD is expressed as mg/L.

Conditioning - Conditioning is the addition of inorganic or organic chemicals to promote coagulation and flocculation of oil or suspended solids, thereby increasing the efficiency of thickening or dewatering processes.

Dewatering - Dewatering is the removal of water from a sludge slurry, usually by mechanical means, to greater than approximately 15 percent solids. At this point, the sludge may behave as a semisolid or solid. The sludge product from a thickening unit would often be the feed for a dewatering unit.

Sludge - The accumulated semi-liquid suspension of settled solids deposited in tanks or basins from raw or treated wastewaters.

Slurry - A suspension of solids in a liquid.

Stabilization - Stabilization is the addition of chemicals, such as lime, diatomaceous earth, fly ash or silicates, which change the consistency of a sludge from liquid to solid. It can be used as an alternative to dewatering, depending on the nature of the sludge and the ultimate disposal method used. The sludge must be fluid enough to mix well with the chemical, but dry enough to prevent excessive chemical use. It is sometimes used following dewatering to pass the paint filter test.

Thickening - Thickening is a process which aims to increase the solids content of a dilute slurry by removing some of the water content by gravitational means. It is commonly used to concentrate biological solids or filter backwash solids where the free water content is greater than 95%, and is usually placed upstream of dewatering processes. The sludge produced is usually pumpable by conventional means and has most of the characteristics of a liquid.

Total Suspended Solids - Total suspended solids (TSS) is the amount of suspended matter removed by a filter paper (which is dried at 217°F (103°C) per unit volume of sludge. TSS is expressed as mg/L.

4.0 BACKGROUND

4.1 GENERAL

Solid waste management can be defined as the systematic reduction, segregation, collection, transport, storage, treatment, recovery, reuse, and disposal of solid wastes. Solid waste management has become increasingly important as the volume of solid waste has increased due, at least in part, to tighter restrictions on air and water qualities. Contaminants removed from the air and water are transferred into dilute slurries which must be concentrated to reduce disposal costs. The storage, transportation, and disposal of wastes needs to follow appropriate local regulations.

4.2 WASTE MANAGEMENT HIERARCHY

Waste management consists of four areas that are often referred to as the Waste Management Hierarchy. These four areas, in order of preference, are: **minimization, recycle/reuse, treatment, and disposal**. Minimization is the preferred method of waste management. By using simple cost effective methods, much of the waste generated within a facility may be avoided. One effective waste minimization technique is the implementation of source control technologies for the reduction of oil and solids to a site's sewer system.

Once all waste minimization techniques have been evaluated, potential waste streams should be evaluated for recycle and reuse opportunities. Many by-product materials that were at one time considered wastes have value in other applications. Sludge coking is one example of reuse wherein hydrocarbon contained within residual material is recovered and the residual solids are incorporated into the coke product. The cascade or reuse of spent caustic and catalyst has also proven effective. For instance, the concentration at which caustic becomes spent on one unit may be fixed, but the spent caustic from that unit may be suitable to use as the caustic feed to another unit. Many recycle methods have also become economic. Many spent catalysts are reclaimed for precious metals. Acids and activated carbon are also being reclaimed.

Treatment is often applied prior to recycle or reuse petroleum processing byproducts. Treatment is also used to reduce disposal costs if recycle or reuse options are not feasible. The treatment of solid or liquid wastes for disposal typically involves volume reduction. By concentrating the solids or contaminants within a waste and reducing the amount of water, the total volume is reduced, thus decreasing overhaul and/or disposal costs. Treatment may also include recovery of valuable hydrocarbon for re-processing.

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4.0 BACKGROUND (cont.)

The final disposition option to be considered for liquid and solid wastes is disposal. Waste disposal is typically costly and should only be used if methods such as minimization and recycle/reuse are not available or not economically justified.

4.3 MATERIAL CHARACTERIZATION

Identification of all solid and liquid waste streams and their current disposition is the essential precursor to determine environmentally acceptable recycle, reuse, treatment, and disposal methods. The mechanisms by which the wastes are generated should be reviewed to see if there are any ways to reduce or eliminate the wastes (for example, the use of cutting oils and centrifuges rather than water and simpler solids separation technique in tank cleaning operations).

A listing of many of the sludges, solid and liquid wastes found in refineries and chemical plants is shown in [Table 1](#).

4.3.1 SLUDGE AND SLURRY

Sludge characterization data is required to determine a suitable waste treatment process such as thickening, dewatering, or thermal treatment. The key properties are water, and solids, and oil content, and whether the sludge can be pumped. Other properties such as pH and Total Organic Carbon (TOC) are useful but not initially required.

The type of sludge should be considered when reviewing analytical data. The wasted biomass (bacterial population) from biological activated sludge treatment system has unique properties not seen in other waste sludges, such as API separator sludge. The bacteria are living organisms which are predominantly water bound within a cellular membrane. Only the free water in which the biomass is transported can be removed by thickening or dewatering, not the bound water within the biomass itself. However, analysis of biomass solids using the Total Suspended Solids (TSS) analytical method, breaks open the cells and releases the bound water within the biomass; both the free water and the formerly bound biomass body water will be evaporated by the TSS test. Review of the analysis alone might indicate that the biomass is dilute (because the cells have been broken) and is fluid, whereas the sample itself may exhibit the physical properties of a solid which cannot be pumped. For instance, a biomass sample with 15 wt% solids content may not be pumped, whereas a non-biological oily waste containing 15 wt% solids could be pumped. Care must be taken when reviewing sludge waste qualities due to this issue.

4.3.2 SOLID MATERIAL

The original purpose or use of the solid material (for example, Cat. plant catalyst) and the Material Safety Data Sheet (MSDS) or equivalent will provide the first broad characterization data and analytical needs, such as metal content. Discussion with personnel from the operating area may also provide information on other qualities. Laboratory analyses including organics (e.g., Volatile Suspended Solids, Total Organic Carbon) and inorganics (e.g., metals -- Fe, Zn, V, Al, Cr) will determine the bulk of the solid waste characterization.

4.3.3 LIQUID MATERIAL

The origin of the liquid before it became a waste and its MSDS will generally provide the rationale for what is required for characterization. However, other trace contaminants (oil content, TOC, TSS), water content, and pH could be equally important. For example, if caustic is used to remove specific sulfur compounds (sulfide, mercaptans) then sulfide and mercaptide will be key parameters to analyze for.

Further laboratory analysis will probably be required to characterize the specific waste either for further processing needs or to comply with local or federal disposal regulations.

4.4 BEST PRACTICES

It has been recognized within ExxonMobil that cost savings and operations improvements at one plant can often be achieved by adopting innovative practices that have been demonstrated at other locations. In the late 1990's several practices were identified as the Preferred Operating Practices (POPs) for waste management. The characteristics that define the POPs are practices which are widely applicable, not merely some piece of equipment, not simply what everyone seems to be doing, high potential to be cost effective, demonstrated and proven, specific, "solution oriented," and consistent with affiliate operating needs and practices.

Fifteen POPs are sited in the following seven areas within the Waste Management Preferred Operating Practices (See Reference 16).

- Site-wide Waste Management

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4.0 BACKGROUND (cont.)

- Minimizing Oil to Sewers
- Reducing Solids to Servers
- Managing Turnaround Waste
- Handling Tank Cleaning Sludge
- Managing Spent Caustic
- Handling Contaminated Soils

For detailed description of these practices, refer to the Waste Management Preferred Operating Practices (See Reference 16). Further Best Practices will be shared via the Water and Waste BestNet.

5.0 MINIMIZATION

5.1 GENERAL

The importance of in-plant waste reduction cannot be overemphasized. The most effective waste management strategy is to prevent wastes from ever forming. Minimization and source control techniques should be used whenever feasible to reduce the amount of waste produced. Large reductions in waste generation are often achievable by increasing employee environmental awareness and/or with procedural changes at minimal expense.

An additional point to remember is that it is more economical to prevent unnecessary dilution since each subsequent concentration step (thickening and/or dewatering) adds to the cost of treatment. It is generally more effective, and less expensive to collect and treat a small, concentrated waste stream than one that is large and dilute.

5.2 SOURCE CONTROL

Source control is often the most effective way to decrease a site's waste management costs by preventing materials from ever becoming a waste. Oil and solids entering into a site's sewer system are major contributors to waste production. Solids (e.g. dirt, gravel, erosion solids, catalyst, coke fines, etc.) entering into the sewer will greatly increase the quantity of primary separator and sewer sludges. Oil that is discharged into the sewer will increase waste production by mixing with solids, creating large quantities of primary sludges as well as increasing secondary sludge production. Studies (References 4 and 11) have shown that a ton of solids entering a sewer will produce five to ten tons of oily sludge.

No Oil to the Sewer - Reference 7 is a comprehensive catalog outlining methods used within ExxonMobil refineries and chemical plants world-wide to reduce or eliminate sources of oil to the sewer. The catalog contains 40 catalog entries focusing on establishing a no/minimal oil to sewer program, communication techniques, proven field practices, and available tools.

No Solids to the Sewer – Reference 4 lists a comprehensive inventory of over 225, mostly at-source, waste reduction technologies currently being used in the industry and their applications within ExxonMobil. In addition, a general method for conducting a waste reduction study and test results at the Port Jerome Refinery are summarized.

Reference 9 is a summary of the different silt screens and catch basin inserts used within ExxonMobil facilities to reduce the amount of solids entering the sewer. Information regarding construction, maintenance, and potential cost savings, due to reduced sludge production, is provided.

5.3 SPENT CAUSTIC USE

Minimization of spent caustic volume may be achieved by either replacing the caustic system with a system that will accomplish the same goal or by optimizing the current caustic system.

Optimizing the current caustic system can be achieved simply through operator training, improved awareness, and attention to operating parameters. Inefficient contacting and inadequate contacting times will lead to non-optimum exhaustion of the available caustic alkalinity. Optimization will clearly produce a more contaminated spent caustic.

Technologies to replace the caustic systems or minimize spent caustic generation are available. Examples of such technologies are: H₂S removal by amine pre-treatment, UOP's Merox® Processes, Merichem's Thiolex, switch from NaOH to KOH, molecular sieves, and oxidation of H₂S to elemental sulfur. Detailed of these technologies are explained in [Design Practice XX-C4](#).

5.4 TANK SLUDGE

There are many techniques used to reduce the amount of tank sludges produced. Techniques include routine activities (e.g. mixers) and advanced cleaning methods (e.g. jet nozzles, simulated mixing and reprocessing tank bottoms (SMART), remote control dredging). Reference 13 contains further detail regarding available methods for cleaning and minimizing tank sludges.