Alternatives in Air Emission Modeling for Characterization of Processes & Process Change

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As facilities prepare for the requirements of Title V of the Clean Air Act, and as permissible exposure limits (PEL) under OSHA continue to decrease, effective means of modeling process air emissions become increasingly important. To date, the focus of air modeling has been to establish the effects of process emissions after they leave the plant, or on the effect of exposures to employees over various time intervals, assuming particular concentrations. Most current techniques are not readily adaptable to assess potential emissions from process changes. The available techniques generally need empirical concentration data to perform the modeling. This paper will examine the strengths and weaknesses of various modeling techniques used for estimating process emissions. Building on this information, a framework will be developed to assist in predicting process emissions that does not rely on empirical data and would therefore be of use in process design.

The analysis of a procedure to incorporate process changes, or design a new process, comprises many factors. Currently, many facilities are considering process changes driven by environmental and health regulations. Incorporating changes that improve the facilities' environmental, health or safety performance can, if implemented properly, also benefit productivity.[1-3] By implementing a pollution prevention program to reduce waste emissions of all media, or the raw material usage, facilities can meet the goals specified by the regulations, with minimal impact on profitability and often actual improvement of the bottom line.

Title V of the Clean Air Act and OSHA Permissible Exposure Limits (PEL) are drivers focused on air emissions. Effective modeling of process air emissions is extremely important if facilities are to meet the goals specified by these regulations. Determining applicability to Title V, which triggers the requirement to prepare a Part 70 permit application, requires a detailed assessment of the facility emissions. Applicability is based on the facility's "potential to emit," that is, the facility's theoretical maximum emissions from all sources. Failure to accurately assess emissions can cast doubt on the applicability of Title V to a particular facility. Many facilities have major source potential to emit, but actual emissions are well below major source thresholds. Accurate modeling of emissions can allow these facilities to opt out of the program with a synthetic minor, usually by accepting a limitation on material usage. For example, a facility fires heating boilers with fuel oil. Boiler capacity is quite large compared to actual utilization and the facility has ~1000 horsepower of boiler heating capacity. This capacity has a potential to emit, with #2 fuel oil, more than 100 tons per year (TPY) of SOx. Actual emissions are probably around 15 TPY. This facility could accept a synthetic minor by agreeing to use only enough fuel to emit 30 TPY total and would not be subject to Title V. Fees to support the program are assessed based on actual facility emissions; however, these fees generally pale before the plant cost of administering the program.

Developing an accurate model to assess emissions for new processes is key to design of emission control or recovery equipment. Virtually all new processes will be required to incorporate equipment that represents MACT (Maximum Achievable Control Technology). Over-design adds unnecessary cost and excess capacity that may never be utilized, while under-design leads to performance failures and significant additional costs to correct improper designs.

Process Analysis

Some view the requirements of Title V as being quite burdensome, and the same can be said of the lower exposure requirements being implemented by OSHA. From a process point of view, however, Title V forces facilities to apply the same rigor used in process control to determine the levels of pollution emitted. OSHA requires regular documentation of the testing completed to verify exposures below hazardous levels. To meet these requirements effectively, formalization of the procedures used regarding work practices and operation of control devices is required in the same way that facilities formalize production operations. In the case of Title V, this is a written requirement.

To date, the focus of quantifying air emissions, and the modeling associated with these tasks, has been to establish the effects of process emissions after they leave the plant or on the effect of exposures to employees assuming particular concentrations.[4,5] Most current techniques are not readily employed to assess emissions for potential process changes, primarily because of the general need to supply empirical concentration data for the various modeling techniques. Clearly for new processes, actual emission data is not available and would necessarily be derived from similar processes or physical property data. This increases the potential for either over- or under-estimating emissions and consequently over- or under-designing process equipment. Before process changes may be effectively designed, data must be obtained that is capable of predicting the effect of those changes relative to the various causes of change.

Understanding process flow in the facility and the factors outside of the immediate process area that can affect the process at hand, helps provide the data necessary to determine the real magnitude of the proposed change. A key element of process analysis is detailed documentation of process procedures. Operating procedures detail the process steps and the key parameters that are monitored to insure the proper functioning of the process. Process procedures can also be used as a repository of the evolutionary history of the process by indicating the type and reason for past changes. Full process understanding includes the ability to demonstrate process control by measuring the key process indicators.

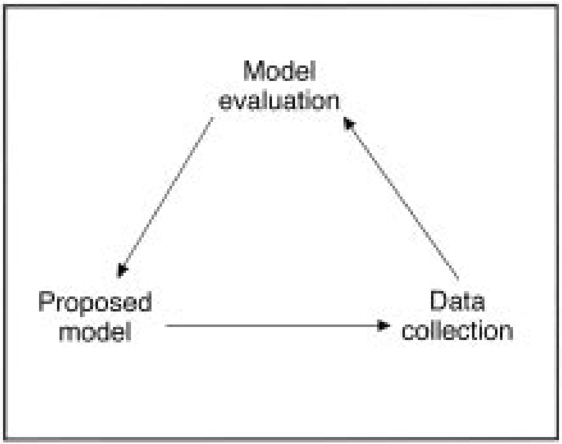

Fig. 1—Process analysis flow diagram.

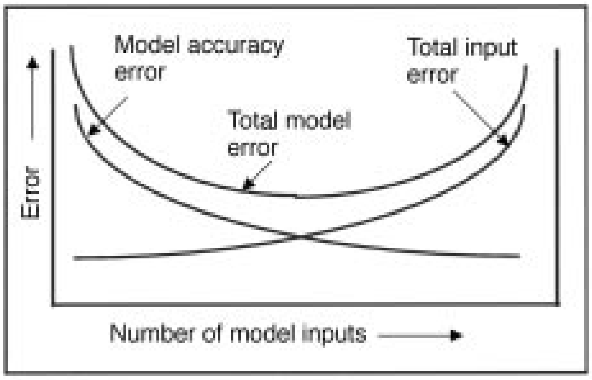

Fig. 2—Process modeling error as functions of complexity and input error.

Developing an Emissions Model

Because each facility's processes have unique qualities, models usually must be adapted. It is very important that a great deal of thought go into the development of emission models. Analysis is generally limited either by time, money, or both, so analysis takes on a cyclic aspect similar to applying a successive approximation technique. This is illustrated in Fig. 1, where first a model is proposed and the data necessary defined. The data are collected and used in the model, then evaluated to determine whether the model really reflects the operation of the process. Modifications to the original model are incorporated as the cycle restarts and this process continues until a satisfactory model emerges or time and/or money constraints force forward motion with a lesser model.

The model needs to have enough inputs to portray the process accurately; however, too many inputs complicate the analysis needlessly and can actually decrease accuracy. This is illustrated in Fig. 2, where it is shown that as the complexity and the number of inputs increases, the model can show a more accurate picture of the actual process. Each piece of data used in the model also has some measurement error associated with it and therefore as model complexity increases, and the number of inputs, eventually the input errors overshadow the accuracy of the model and total error increases. Figure 2 illustrates that there is an optimum number of inputs, which provides the best accuracy and minimizes the input error component.

Modeling may most effectively be accomplished in phases, where a coarse screening model is initially employed to determine applicability and, if necessary, a more detailed model is then used to more fully quantify process emissions. For some variables, rough estimates may be perfectly acceptable. Cost information needs to be considered as a leveling factor for the amount of effort that must be expended. In general, a little extra cost up front in the modeling and design phase will pay dividends in the long run by more accurately sizing equipment, which will optimize operating costs. The gains from modeling are limited generally as a function of the size, complexity, variability and uniqueness of the process and the potential for future process changes.

Techniques Available

Mass Balance

Constructing mass balance for a process can be a very powerful tool in assessing emissions if all of the process inputs and outputs can be characterized. Often, air emissions are difficult to measure directly and are consequently inferred from quantifying the other inputs and outputs. Data collection begins by gathering information on the quantity of raw materials used, the quantity of material incorporated in the finished product, and information on the waste generated. Figure 3 shows pictorially the information needed. Waste is divided into three areas: solid waste, wastewater emissions, and air. That is:

$$M_{RAW} = M_{PROD} + M_{SWASTE} + M_{AWASTE} + M_{H_2OWASTE} \qquad (1)$$

where M_{RAW} is the raw material used, M_{PROD} is the amount of raw material incorporated in the product, M_{SWASTE} is the raw material in the solid waste generated, M_{AWASTE} is the raw material released as air emissions, and $M_{H_2OWASTE}$ is the raw material released in wastewater.

Mass balances are most effective when the process quantities are small and can accurately be measured, or when the process is relatively simple. For example, the use of isopropyl alcohol in an assembly area is relatively easy to assess, because the material either ends up in a waste collection area or it evaporates as it is used. Large production quantities of materials in use introduce measurement difficulties that lower the accuracy. These difficulties arise from establishing an accurate inventory of the in-process materials that have left stock but have not been used in the manufacturing process.

While defining the data needed to complete a mass balance may seem trivial, actually collecting the data is anything but

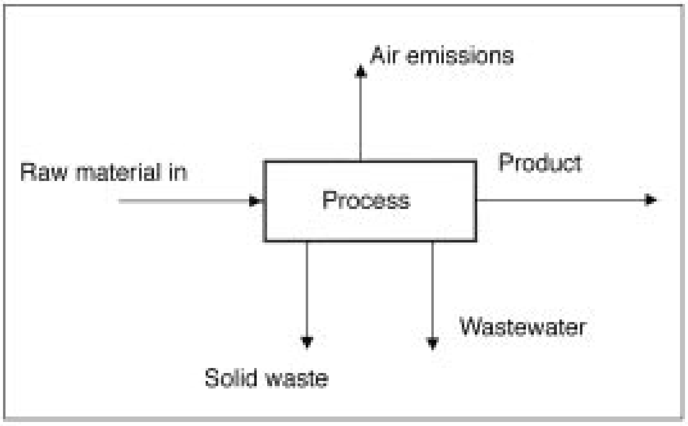

Fig. 3—Process material input/outputs.

trivial. For example, consider a paint booth operation. The quantity of paint used is known accurately from the stores log and is released to the floor in gallon quantities. The paint is applied to parts in a spray booth equipped with a water curtain scrubber. This water is treated and released. Treatment sludge is shipped as hazardous waste. There are seven other spray booths in the company. The spray guns are cleaned in enclosed cleaners equipped with solvent sumps. Several difficulties exist in collecting the data to complete a mass balance for the process. These difficulties can be seen by considering some questions relating to this process, the materials used and the waste generated.

- How much paint is used to coat the parts?
- How much paint is lost in gun cleaning?
- What is the capture efficiency of the spray booth hood?
- How does production in this spray booth compare with the others?
- How much of the treatment sludge generated is paint related?
- What other organic sources contribute to the wastewater released?

The answers to those questions can often determine the effectiveness of the mass balance. A sampling of the parts painted can be weighed before and after to determine the coating weight. If necessary, the weight could be further analyzed for average thickness by determining the part surface area. Paint lost to gun cleaning can be determined if the solvent loss of the gun cleaning equipment is known, and accounting for the weight increase of the solvent in the sump over a specified number of gun cleanings. Capture efficiency is specified by the manufacturer and may be verified by operational testing. Production logs can be used to determine the production through this hood relative to others and this information used to partition both the sludge generation and the organic contamination in the released waste water.

One further question must be answered: Is all of this information necessary for the mass balance? Maybe. Using wastewater as an example, assume that the facility releases 10,000 gal/day wastewater with a 10 ppm organic solvent concentration related to paint booth operation. This concentration translates into a total release of just over 200 lb/yr for all the paint booths. If emissions from this process are in the 10 TPY range, this quantity in the wastewater represents ~1 percent of the air emissions associated with the process. This quantity then has limited effect on both the air emissions and on the mass balance as a whole, and could be omitted from the mass balance to streamline the model. This determination does point to a key element of designing the model used to evaluate the process, as discussed earlier, and that is understanding the process drivers. In this case, the wastewater emissions may be an insignificant term in the mass balance; however, that determination cannot be made without a clear understanding of the process and the magnitude of the various components.

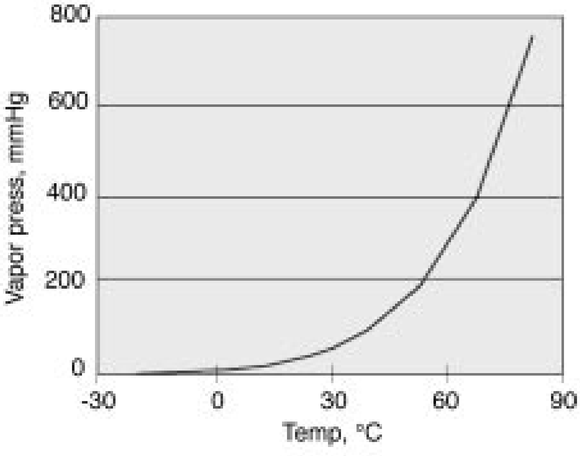

Fig. 4—Plot of vapor pressure vs. temperature for isopropyl alcohol.
(Perry's Chemical Engineer's Handbook, 4th Ed.)

Vapor Pressure

The use of vapor pressure data is another method of estimating process air emissions. All liquids and some solids have vapor pressures created as the substance spontaneously converts from the liquid phase to the gas phase. Vapor pressure is very strongly dependent on temperature. Effective use of vapor pressure data requires knowledge of the process solution temperature. Figure 4 shows a plot of vapor pressure vs. temperature for isopropyl alcohol. In mixtures, the solvents generally tend to vaporize as if they were the only component present. This is sometimes modified if there are chemical interactions between the components of the mixture. For most solvent systems, however, vapor is formed in very nearly an ideal manner (in terms of the ideal gas law) and variations will not be noticeable. One key condition is that the vapor loss must leave the solution concentration unchanged. Because process tanks generally have large liquid volumes relative to evaporation and receive regular additions, this is generally a safe assumption.

Figure 5 shows plots of the vapor pressure of three common paint solvents vs. temperature. From Dalton's Law of Partial Pressures, the individual vapor pressures of the component mixture add (water vapor included) to create the total vapor pressure above a process vessel.

$$P_T = P_1 + P_2 + ... + P_X \qquad (2)$$

One way of using vapor pressure data is to determine the fraction of vapor lost that is partitioned to the various solvents used in a process. For example, a paint gun cleaning operation uses 1000 gal of solvent mixture for cleaning painting equipment and determines through a mass balance that 1000 lb of solvent are lost from the cleaning operation because of

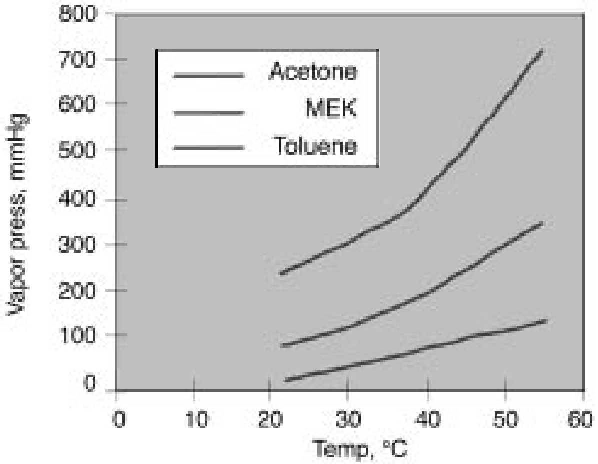

Fig. 5—Plot of vapor pressure vs. temp for various paint solvents.
(Perry's Chemical Engineer's Handbook, 4th Ed.)

evaporation. The paint solvents are composed only of methyl ethyl ketone (MEK) and toluene. The ratio of the solvents is 2:1 toluene to MEK. Initially, it might be said that ~670 lb of the loss are toluene; however, consideration of the vapor pressure discloses a different result.

Evaporation is occurring at room temperature 70 °F (21 °C). From Fig. 5, the vapor pressure of toluene and MEK at 21 °C are 10 and 90 mmHg, respectively. The fraction of the vapor escaping is defined below.

$$Vf_{MEK} = VP_{MEK}/VP_{TOTAL} \quad (3)$$

$$Vf_{Toluene} = VP_{Toluene}/VP_{TOTAL} \quad (4)$$

Where Vf is the vapor fraction of either MEK or toluene and VP is the vapor pressure of the species of interest and VP_{TOTAL} is the total vapor pressure of the system [Eq. (5)]:

$$VP_{TOTAL} = VP_{MEK} + VP_{Toluene} \quad (5)$$

Water vapor is neglected because evaporation of these components is independent of the humidity.

From Eqs. (3) and (4), the vapor fractions of the two solvents are defined; however, to assign mass to the components, further calculation is required. From the ideal gas law, the pressure of a gas is proportional to the number of molecules of that gas present. Equation (6) illustrates this:

$$P_{MEK} = VP_{MEK} = \frac{n_{MEK}RT}{V} \quad (6)$$

where n_{MEK} is the number of moles of MEK present, R is the ideal gas constant, T is temperature in °K and V is the volume of the gas. If the volume and temperature of the system are held constant, Eq. (6) becomes

$$\frac{P_{MEK}}{n_{MEK}} = C \quad (7)$$

where the constant C combines R, T and V. This is also true for a mixture of gases if the volume and temperature are held constant. The vapor fractions calculated in Eqs. (3) and (4) are proportional to the mole fraction of each vapor. Multiplying by the molecular weight of each substance yields the total mass of each compound emitted for a given volume of total vapor lost. This datum allows calculation of the mass fraction of the vapor to partition the relative losses of each solvent.

$$Vf_{MEK} = 0.90 \text{ mol } (72 \text{ g/mol}) = 64.8 \text{ g} \quad (8)$$

$$Vf_{Toluene} = 0.10 \text{ mol } (92 \text{ g/mol}) = -9.2 \text{ g} \quad (9)$$

$$Wf_{MEK} = 64.8/(64.8 + 9.2) = 0.87 \quad (10)$$

$$Wf_{Toluene} = 9.2/(64.8 + 9.2) = 0.13 \quad (11)$$

The mass of MEK and toluene released is determined by multiplying the mass fractions calculated in Eqs. (10) and (11) by the mass-balance-derived solvent release from the process of 1000 lb.

$$\text{Mass MEK released} = 0.87 \text{ (1000 lb)} = 870 \text{ lb} \quad (12)$$

$$\text{Mass toluene released} = 0.13 \text{ (1000 lb)} = 130 \text{ lb} \quad (13)$$

Equations (12) and (13) indicate that a considerably different release of the solvents would be estimated from strict use of the composition of the solution.

Vapor pressure worked well to augment results of a mass balance for solvent losses. The use of vapor pressure is not as straightforward for estimating emissions from some process tanks. For example, evaporation from plating tanks is nearly all water and can contain other volatile substances, such as acids. Difficulty in estimating emissions arises from the fact that regulatory levels for the hazardous components are quite low and that they comprise a small fraction of the evaporation loss. In addition, ventilation systems are designed to remove large quantities of air to the outside and prevent the formation of hazardous atmospheres.

The removal of air mechanically in the ductwork causes a drop in pressure at the hood slot. The molecules of gas composing the air move to equilibrate the pressure drop. Their motion becomes less random and, at steady state, forms a stream of air across the top of the tank. The average molecular velocity of air is ~10^4 cm/sec (328 ft/sec) at room temperature.[6] Air movement above a process tank is considerably slower than the molecular speed and is typically in the range of 50 to 100 ft/min. This moving stream captures the hazardous vapors or mists that leave the tank surface and attempt to diffuse randomly away.[7] The farther from the slot, however, the less coherent the stream and diffusion becomes more random.[8] Capture velocities are calculated to maintain sufficient air movement to capture vapors and mists at the remote areas of the process vessel. An excellent mathematical treatment of particle capture is given in Ref. 9. The model developed therein calculates capture trajectories based on emitted particle velocity. Movement of the air through the system is generally characterized by the volume of air moved per unit time (ft^3/min).

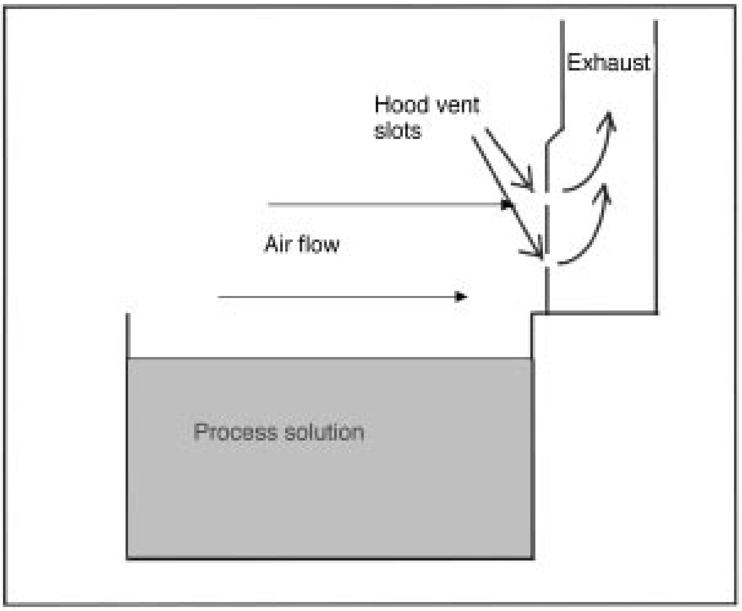

Fig. 6—Process tank with ventilation schematic.

Calculating emissions from these process tanks can be accomplished by considering the removal rate of the air through the ventilation system and the vapor pressure of the substance of interest. The weakness of the calculations of emissions by this technique is that it assumes all air removed by the system is saturated with the vapor from the process tank, which is not necessarily true.

Figure 6 illustrates the capture of vapors by the ventilation system. For any given process at various conditions of volatility and temperature, a unique steady-state concentration of vapor will develop in the air stream. The exact concentration would depend on particle mass, and the temperature of the solution. Vapor diffusion is directly proportional to the molecular velocity, which in turn is directly proportional to temperature and inversely proportional to particle mass. Hotter, smaller particles will, therefore, more completely populate the capture zone depicted in Fig. 7. Because the goal of local exhaust is to capture all of the hazardous emissions, a properly designed hood would not allow any particles to diffuse completely through the capture zone; therefore, the air removed by the system would not be completely saturated with process vapors. Calculations made in this way would then be worst-case emissions for the process. As with organic solvent evaporation, evaporation of the acid must leave the solution concentration essentially unchanged.

As an example, consider nitric acid used in a stripping operation at a concentration of 50 wt pct HNO_3. The tank is operated at room temperature (20 °C), giving nitric acid a vapor pressure of 0.27 mmHg. The ventilation system removes 1000 cfm of air from this tank. Tank emissions for 24 hr are determined by calculating the mass of nitric acid per unit volume of air removed. This quantity is scaled to the total amount of air removed for the time period. The quantity of nitric acid in a 1.0 liter volume, at 0.27 mmHg, is given by the ideal gas equation:

$$PV = nRT \qquad (14)$$

where P is the pressure in atmospheres, V is volume in liters, n is the number of moles of nitric acid present, R is the ideal gas constant, 0.082 L-atm/deg K mole, and T is the temperature in °K.

$$\frac{0.27 \text{ mmHg } (1.0 \text{ L})}{760 \text{ mmHg/atm}} = n(0.082 \text{ L-atm/deg K mole}) (293 \text{ K}) \qquad (15)$$

$$n = 1.48 \times 10^{-5} \text{ mole}$$

Converting to the mass of nitric acid is accomplished by multiplying the moles of nitric acid by the molecular weight of 63 grams/mole.

$$1.48 \times 10^{-5} \text{ mol} \times 63 \text{ g/mol} = 9.32 \times 10^{-4} \text{ g} \qquad (16)$$

Each liter of air exhausted from this process tank then contains 9.32×10^{-4} g of nitric acid. There are 28.3 L in a cubic foot. Eq. (16) becomes

$$9.32 \times 10^{-4} \text{ g/L } (28.3 \text{ L/ft}^3 = 2.6 \times 10^{-2} \text{ g/ft}^3) \qquad (17)$$

The resulting 24-hr release is 82.6 lb of nitric acid/day from this process.

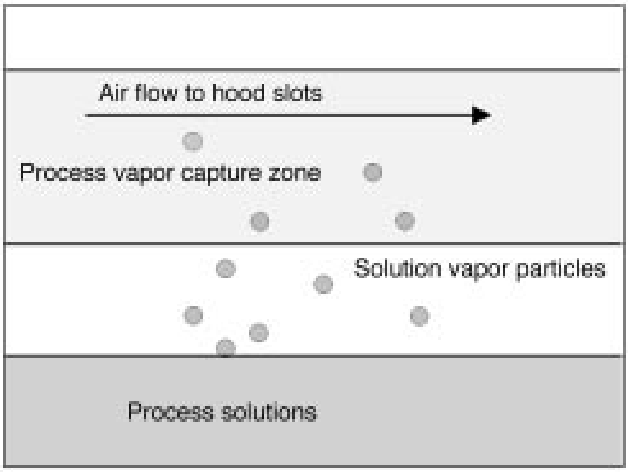

Fig. 7—Hood ventilation capture of process vapor or mist emissions.

The nitric acid calculation assumed complete saturation of the exhausted air stream. What is the actual percent acid vapor present? Vapor pressures of some substances cannot be measured directly, such as sulfuric acid, and require more elaborate means of calculation, or the solution properties may cause a deviation from the ideal. The deviation changes evaporation and must be accounted for in emissions estimates. The advances in desktop computing make a relatively simple computer problem out of what was a very time-consuming hand calculation requiring successive approximations.

Solutions that emit aspirated droplets containing hazardous material are even more difficult for estimation of emissions. The situation is further complicated if the process vessel is air-agitated, which alters the evaporation rate and can also cause drops of solution to be ejected from the solution as aerosols. In these cases, many have opted to use emission factors rather than attempt difficult calculation exercises to estimate the emissions from the processes.

Emission Factors

Emission factors can provide a relatively quick, effective mechanism for estimating difficult process emissions. Emission factors are developed by gathering quantities of data on the processes and developing trends for the process, based on some easily measured parameters. The accuracy of the emission factor depends on

- the similarities of the various data collected
- the quality of the experiments used to collect the data
- similarity of the process to the process from which the emission factor was derived

One area in which emission factors are used with higher confidence is in the estimation of heavy metal hazardous air pollutant (HAP) emissions from the combustion of fossil fuels. The chief repository of emission factors is the U.S. EPA document AP-42. This document sees so much use that it is available from the government printing office on CD-ROM. Care must be used in evaluating the relevance of emissions calculated with emission factors, because design problems can arise if the limitations of the results are not clearly understood.

Many electroplating solutions produce emissions that arise chiefly from the formation of aerosols, and these are particularly difficult to estimate. This is true both of estimating the evolution of particles into the exhaust stream and in modeling the effect of the control equipment on the released droplets. The source of these aerosols can be either chemical, for example, the release of hydrogen from the interaction of aluminum with sodium hydroxide during caustic etching, or they may be electrochemical. Inefficiencies in various electroplating processes are well known to result in electrolysis of water, releasing hydrogen and oxygen at the electrodes. The gas released from the tank surface forms microscopic bubbles of the process solution above the process bath. The bubbles eventually collapse into droplets which must be captured. The droplet size created is a function of the colligative properties of the process solution and the velocity of the exit gas stream above the process solution.[10] Modeling of the droplets is difficult because their formation varies as a function of the bath composition and the applied current. Because of these difficulties, emission factors are generally used to estimate emissions. The results obtained must be interpreted cautiously for system design purposes.

For example, an aerospace manufacturer was building a new captive plating shop in an area where very stringent chromium emission standards predated the chromium electroplating NESHAP. The manufacturer could not operate the new anodizing process without installing a scrubber. The appropriate emission factor for estimating chromium emissions from chromic acid anodizing was 2.0 mg/A-hr of operation.[11] Emissions of chromium mist are estimated by using the emission factor, coupled with rectifier current and hours of operation (Eq. 18).

$$E_{Cr} = F_{Cr}(R_I)(R_T)(C_{eff}) \qquad (18)$$

where E_{Cr} is the estimated chromium emission in mass per unit time, F_{Cr} is the emission factor for chromic acid, R_I is rectifier current, R_T is the hours of rectifier operation within the emission time period, and the final term, C_{eff}, is control device efficiency and is equal to (1-eff.). Substituting values for the terms, including a 99.95 percent control efficiency; converting to pounds yields Eq. (19).

$$\text{(2 mg/amp hr)(500 A)(8 hr)(0.0005)}(2.2 \times 10^{-6}\text{ lb/mg}) = 8.8 \times 10^{-6}\text{ lb/8 hr} \qquad (19)$$

Equation (19) assumes continuous operation over the eight-hr time period at maximum current. This did not reflect expected process operation; therefore, the calculation was further refined to reflect expected operating parameters. Operator logs indicated that maximum operating current in the old facility was 200 A. The new facility's chromic acid anodizing tank had a 40-percent greater capacity, and this was used in increasing the maximum operating current to 300 A. The chromic acid anodizing line is not a dedicated line and other types of anodizing are also run in this line. Actual operation of the rectifier was only 2.4 hr/8 hrs. Equation (19) then becomes

$$\text{2 mg/amp hr(300 A)(2.4 hr/8 hr)}(2.2 \times 10^{-6}\text{ lb/mg})(0.0005) = 1.58 \times 10^{-6}\text{ lb/8 hr} \qquad (20)$$

This emission loading was then used by the manufacturer for final sizing of the scrubber and operational testing was performed. The unit failed to meet the state limit of ~$7\text{x}10^{-6}$ lb/8 hr. After approximately two years of discussions and evaluation of the unit with the manufacturer and regulators, it was determined that the loading on the unit was so low that the droplets captured by the mesh pads were drying and being released as dust. The unit was then refitted with an HEPA filter to capture these particles. Performance testing of the unit has not yet been completed.

Emission factor calculations for the unit were not used blindly. Several methods for estimating emissions were examined and the calculations refined to reflect the actual operating conditions expected. In addition, an independent review of the design was commissioned. This review resulted in a down-sized system as non-emitting process tanks were eliminated from scrubbing. The down-sizing cut the unit capacity by approximately 50 percent, but even this review failed to predict the system load accurately. Much additional cost has been incurred in analyzing and correcting the problem; far more than the unit cost. This example also points out quite clearly that more is not necessarily better in process design. The additional capacity over the actual loading results in drying of the particles. Dusts are then emitted that are not captured by the mesh pads. The example also indicates that there is a need for accurate methods to predict emissions for new process installations.

Exposure Data

Exposure sampling can result in concentration data by a variety of means that are also useful in emission calculations. These data are especially useful when a process is upgraded from having no control to a controlled state. As an example, emissions of cadmium from a welding operation will be discussed.

A facility is a major source under Title V of the Clean Air Act. The facility must quantify the emissions of all HAPs as part of preparing its Part 70 permit application. Area testing in the welding shop via personal samplers indicates cadmium concentrations of 0.05 mg/m^3 average for the two shifts of operation. Current room ventilation is 100 cfm. Assuming that 700 cfm will take the concentration down below the PEL[12] of 0.005 mg/m^3, what will the emissions from this process contribute to the total HAP emissions for the facility?

To solve this problem, the current rate of cadmium emission must be calculated because the data represent steady state conditions with exhaust of 100 cfm. The room volume is needed. That volume is 1500 ft^3 and the total room volume of air is turned over every 15 min. The room's concentration of cadmium is 0.05 mg/m^3 and, assuming that this concentration is a steady-state value, the total cadmium released per min by the welding process must exactly equal the amount removed. The amount removed is

$$M_{Cd} = (100\ \text{ft}^3/\text{min})(1/35.3\ \text{ft}^3/\text{m}^3)(0.05\ \text{mg/m}^3) = 1.41\ \text{mg/min}. \qquad (21)$$

Welding is done over two shifts, or 16 hr, and daily emissions are given by Eq. (22).

$$\begin{aligned} M_{Cd} &= (1.41\ \text{mg/min})(60\ \text{min/hr})(16\ \text{hr/day})(1000\ \text{mg/g}) \\ &= 1.35\ \text{g/day} \qquad (22) \end{aligned}$$

It should be recognized that removal of the contaminant would occur over a greater time than the 16 hr of the twoshifts because it takes some time to reach steady state and for the ventilation to completely clear the room after cessation of welding activities at the end of the second shift. The point is that exposure data taken to assess worker safety can be used in certain cases to estimate process emissions. In some cases, estimating emissions requires the solution of difficult mathematical models; however, if the process outputs can be simplified or isolated, generally simple differential equations can be used to model output emissions.

Process Design Model

Clearly, estimating emissions for new process installations is extremely important. The results of poorly defined models can lead to equipment designs that do not meet regulatory requirements, either from the standpoint of worker safety or the emission levels specified under the Clean Air Act.

As discussed earlier, process analysis and process design are cyclical activities where successive approximations (models) about the nature of the process are made and evaluated. These models are either accepted, improved, or discarded. Deciding on the necessary level of detail and the relative sophistication of the analysis depends on many factors that are considered at various stages of the evaluation. Some factors, especially those involving goals and cost, will be revisited several times as the design process is honed. Among these process design factors are the following:

- What is the goal of the design?
- Are the design drivers product, environmental or safety related?
- How does over- or under-design affect the operational cost?
- Can under- or over-design of the process result in process failure?
- If over-designed, is the additional capacity likely to be utilized?

These questions attempt to identify the key parameters driving the design analysis. They help develop the scope of the effort from a “big picture” point-of-view and lay the groundwork for subsequent detailed analysis.

Once these questions have been answered and drivers, direction and goals established, the process model/emission estimation poses additional questions to focus the design.

- What level of accuracy is really necessary in the model?
- What is the cost of the needed level of accuracy?
- What kinds of data are currently available?
- What level of accuracy do the available data allow?

These questions help identify the information to be collected and the relative cost of developing the data. Accuracy and cost, relative to the entire project, should be effectively balanced throughout the course of the design evaluation. Extra dollars spent in design generally can pay big dividends in process operation if the process has a significant useful life, or if subsequent optimization is anticipated. Small gains made in design will pay off over the lifetime of the process. It is important to understand which processes are worthy of extensive analysis to avoid expensive blind alleys that yield little useful data or cost reduction.

Evaluating the kinds of data necessary and available for design often provides feedback into the design process and helps sharpen the focus. Complicated experiments must be carefully designed and may give only slightly better input to the design process than “quick and dirty” methods. Analysis and process understanding go hand-in-hand and detailed experiments should not be attempted without the associated degree of process understanding. Once these questions have been answered, the use of process design simulation tools can be considered. A properly designed model will provide a great deal of information and will allow relatively easy methods of investigating changes and their effect. There are many computer-based tools available; some are intended for design of complex processes, similar to those expected at a large petrochemical plant,[13] others are more focused, looking at surface finishing[14] or facility/process waste emissions.[15]

The hierarchy for evaluating emissions almost always begins with performing simple screening analysis, usually via a mass balance. This is especially true when determining applicability to a regulatory requirement. The mass balance can be made more or less detailed as need dictates. Information for new processes must come either from the former process scaled to the new, or from emission factors. Using this information, process cost is evaluated, as are any applicable environmental, health or safety requirements. These requirements may push analysis to a more detailed level than would production-related criteria. Detailed analysis is now appropriate with a modeling activity based on the chemistry and physics of the process. Many times, analysis need proceed no further than the use of the ideal gas law or Dalton’s Law of Partial Pressures. In certain cases, the chemical stoichiometry will need to be investigated, as in waste treatment design; however, with complex mixtures this is often extremely difficult to accomplish definitively. Estimation of reaction rates can generally be reduced to a first order equation and calculated reasonably simply.

Conclusions

This paper has reviewed methods of estimating air emissions. The quality of the data developed from these emissions estimates depends greatly on in-depth understanding of the process, and can only be as good as the data used to develop the estimates. Often, simple mass balances can be used to develop process emissions effectively. At other times, a more detailed analysis will be required, making use of scientific principles and mathematical modeling techniques. Caution must be exercised to obtain the appropriate level of detail for the analysis.

Emission estimates can be used to develop plans of action to meet various regulatory requirements, and they also provide data of vital use in process design. Examples have been offered that can estimate emissions based on limited or no empirical data therefore, being of use in process design. A clear understanding of the nature of the process is required, however, because each new application of a process poses unique circumstances that must be recognized and quantified for the process design to address them effectively.

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