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What Is Chemical Engineering?

There are no doubt numerous dictionary definitions of chemical engineering that exist. Any of these could be unique to the environment being discussed, but all of them will involve the following in some way:

1) Technology and skills needed to produce a material on a commercially useful scale that involves the use of chemistry either directly or indirectly. This implies that chemistry is being used at a scale that produces materials used in commercial quantities. This definition would include not only the traditional oil, petrochemical, and bulk or specialty chemicals but also the manufacture of such things as vaccines and nuclear materials, which in many cases may be produced in large quantities, but by a government entity without a profit motive, but one based on the welfare of the general public.
2) Technology and skills needed to study how chemical systems interact with the environment and ecological systems. Chemical engineers serve key roles in government agencies regulating the environment as well as our energy systems. They may also serve in an advisory capacity to government officials regarding energy, environmental, transportation, materials, and consumer policies.
3) The analysis of natural and biological systems, in part to produce artificial organs. From a chemical engineering standpoint, a heart is a pump, a kidney is a filter, and arteries and veins are pipes. In many schools, the combination of chemical engineering principles with aspects of biology is known as biochemical or biomedical engineering.

The curriculum in all college-level chemical engineering schools is not necessarily the same, but they would all include these topics in varying degrees of depth:

1) Thermodynamics. This topic relates to the energy release or consumption during a chemical reaction as well as the basic laws of thermodynamics that

Chemical Engineering for Non-Chemical Engineers, First Edition. Jack Hipple.

are universally studied across all fields of science and engineering. It also involves the study and analysis of the stability of chemical systems and the amount of energy contained within them and the energy released in the formation or decomposition of materials and the conditions under which these changes may occur.

2) Transport Processes. How fast do fluids flow? Under what conditions? What kind of equipment is required to move gases and liquids? How much energy is used? How fast does heat move from a hot fluid to a cold fluid inside a heat exchanger? What properties of the liquids and gases affect this rate? What affects the rate at which different materials mix, equilibrate, and transfer between phases? What gas, liquid, and solid properties are important? How much energy is required? Materials do not equilibrate by themselves. There is always a driving force such as a pressure difference, a temperature difference, or a concentration difference. Chemical engineers study these processes, their rates, and what affects them.
3) Reaction Engineering and Reactive Chemicals. Chemical reaction rates vary a great deal. Some occur almost instantaneously (acid/base reactions), while others may take hours or days (curing of plastic resin systems or curing of concrete). A chemical reaction run in a laboratory beaker may be where things start, but in order to be commercially useful, materials must be produced on a larger scale, frequently in a continuous manner, using commercially available raw materials. These industrially used materials may have different quality and physical characteristics than their laboratory cousins. Since most chemical reactions either involve the generation of heat or require the input of heat, the practical means to do this must be chosen from many possible options, but for an industrial operation with the potential of release of hazardous materials, the backup utility system must be clearly defined. In addition, chemical reaction rates are typically logarithmic, not linear (e.g., as is the case with heat transfer), providing the possibility for runaway chemical reaction. Chemical engineers must design operations and equipment for such conditions.
4) Safety. There is no basic difference in the hazards or properties of a substance such as chlorine gas on any scale. Its odor, color, boiling point, and toxicity do not change from a small laboratory canister or cylinder to a 10 000 gallon tank car or bulk cylinders used in municipal drinking water disinfection. However, the release of such a material from large-volume processes and tanks can have disastrous consequences to surrounding communities and the people living around them. Any large chemical complex has the same concern about the materials it uses, handles, and produces to ensure that its operations have minimal negative effects on the surrounding community and its customers. The incorporation of formal safety and reactive chemicals education within the college chemical engineering curriculum is a fairly recent and positive development. Chemical engineers are heavily involved

not only in designing and communicating emergency plans for their operations but also in assisting the surrounding communities' emergency response systems and procedures, including ensuring that the hazardous nature of materials used and processes are well understood.

5) Unit Operations. This is a unique chemical engineering term relating to the generic types of equipment and processes used in scaling up laboratory chemistry and the practice of chemical engineering. Heat transfer would be an example of such a unit operation. The need to cool, heat, condense, and vaporize materials is universal in chemical and material processing. The equations used to estimate the rate at which heat transfer occurs can be generalized into a simple equation such that Q (amount of energy transferred) is proportional to the temperature difference (ΔT) as well as the physical characteristics of the system in which the heat transfer is occurring (mixing, physical property differences such as density and viscosity). This would be expressed mathematically as $Q = UA\Delta T$. The amount of energy transferred and the temperature difference may be known, but the "coefficient" (frequently represented by the letter U) relating the two may vary considerably. However, this basic equation can be applied to any heat transfer situation. The same thoughts apply to many separation unit operations such as distillation, membrane transport, reverse osmosis membranes, chromatography, and other "mass transfer" unit operations. The rate of mass transfer is proportional to a concentration difference and an empirical constant, which will be affected by physical properties, diffusion rates, and agitation. In many chemical plant operations, there is an overlap in these areas. For example, a distillation column will involve both heat and mass transfer. The same is true for an industrial cooling tower. The last of these general topics is fluid flow. Though there are many types of pumps and compressors, they all operate on the same basic principle that says that the rate of flow is proportional to the pressure differential, the energy supplied, and the physical properties of the liquid or gas. Again, there is an overlap, as any equipment of this type is also using energy and heating up the liquid or gas it is moving. The heat transfer, as well as the fluid transfer, must be considered.

6) Process Design, Economics, and Optimization. There are numerous ways of scaling up a chemical production system. The choice of particular separation processes, transport systems, storage systems, heat transfer equipment, mixing vessels, and their agitation systems can be done in various combinations, which will impact reliability, cost, the way the process is controlled, and the uniformity of the output of the process. "Design optimization" is a term frequently used. The "optimum" design will not be the same for all companies making the same product as their raw materials base, customer requirements, energy costs, geographic location, cost of labor, and other company unique variables will affect the decision as to what is optimum.

Our ability to computerize chemical engineering design calculations has greatly enabled chemical engineers' capabilities to evaluate a large number of options.

7) Process Control. In a laboratory environment where small quantities of materials are made, the control system may be rather rudimentary (i.e., an agitated flask and on/off heating jacket). However, when this same reaction is "scaled up" orders of magnitude and possibly from batch to continuous, the nature of the process control changes dramatically. The continuous production of specification material around the clock has special challenges in that the raw materials (now coming from an industrial supplier and not a reagent chemical bottle) will not be uniform, the parameters of utilities needed to heat and cool will not be uniform, and the external environment will constantly change. Chemical engineers must design a control system that will not only have to react to such changes but also ensure that there are minimal effects on the product quality, the outside environment, and the safety of its employees.

As the field of chemical engineering has expanded, many curricula will also contain specialty courses in such areas as materials science, environmental chemistry, and biological sciences. However, even when these specialty applications are "scaled" to commercial size, the aforementioned basics will always be needed and considered.

What Do Chemical Engineers Do?

With this type of training, a unique combination of chemistry, mechanical engineering, and physics, chemical engineers find their skills used in a variety of ways. The following is certainly not an all-inclusive list but represents a majority of careers and assignments of most chemical engineers:

1) The scale-up of new and modified chemical processes to make new materials or lower cost/less environmentally impactful routes to existing materials. This is most often described as "pilot plants," which typically is a middle step between laboratory chemistry and full-scale production. In some cases this can involve multiple levels of scale-up (10/1, 100/1, etc.) depending upon the risk factor and the knowledge that exists. A newly proposed process that has operating issues or causes safety releases in a laboratory environment is a serious issue. If that same problem occurs on a much larger scale, the consequences can be far more severe, simply due to the amount and scale of materials being inventoried and processed. These consequences can easily include severe injuries and death, large property damage, and exposure of the surrounding community to toxic materials.

2) Design of Processes and Process Equipment. It is rare that the equipment used in a full-scale plant is identical in type to that used in the laboratory or possibly even in the pilot plant. The piping size; the number and type of trays in a distillation tower; the configuration of coils, tubes, and baffles in a heat exchanger; the shape and size of an agitator system; the shape and geometry of a solids hopper; the shape and configuration of a chemical reactor; and the depth of packing in a tower are all examples of such detailed design calculations. In the commercial world, there may be limitations of certain speeds, voltages, and piping specifications that may not match exactly with what may be desired from smaller-scale work. In these cases, the chemical engineer, in collaboration with other engineers, needs to design a system that will achieve the desired goals, but within practical limitations. In many large chemical and petrochemical companies, chemical engineers will become experts in a certain type of process equipment design and focus most of their career in one particular area.
3) Though certainly not unique to the domain of chemical engineers, the design of utility support systems for chemical plant operations is critical. This includes the supply of water for process and emergency cooling, continuity of electrical supply for powered process equipment such as pumps and agitators, and supply of oil, gas, or coal to generate steam and power. Options chosen will certainly be affected not only by economics but also by limitations of a particular manufacturing site. These may include water availability, water and air permit limitations, and the reliability of local public utility supplies.
4) Sales and marketing positions in the chemical, petroleum, and materials industries are frequently filled by chemical engineers. The ability to understand the customer's process may be critical to the ability to sell a material to a customer, especially if it is a new material or requires substantial change in a customer's operation.
5) Safety and environmental positions, both within industry and government, are frequently filled by chemical engineers. In order to write rules and regulations, it is important to understand the basic limitations of chemical processes, laws of thermodynamics, and the limits of measurement capabilities. Regulations and enforcement actions relating to hazardous material transport also require chemical engineering expertise, especially in bulk pipeline, rail car, and truckload shipping.
6) Cost estimates in the chemical and petrochemical areas are also done by chemical engineers in conjunction with mechanical, civil, and instrumentation engineers. With the availability of today's computer horsepower, it is possible to evaluate and compare many possible process options as a function of raw material pricing, geographic location, energy cost, and cost projections. This allows optimum process design and the ability to predict process costs and economics under changing conditions.

7) The supervision of actual chemical plant operations is most often done by chemical engineers. In this role, the understanding of equipment design and performance is critical, but more importantly the management of plant operations to minimize safety incidents and environmental releases, as well as complying with permits under which the plant is allowed to operate. In this role chemical engineers have additional unique responsibilities including labor relations with operating plant personnel as well as the need, in some cases, to interface with the surrounding community in a public communications role.
8) In universities and in advanced laboratories within many large corporations, basic chemical engineering research is done by advanced degreed chemical engineers, many times in association with other disciplines. Examples of such work would include chemical engineering principles used in the design of artificial organs (remember: the heart is a pump and the kidney is a filter), the study of atmospheric diffusion to study the impact of environmental emissions, the design and optimization of process control algorithms, alternative energy sources and processes, and the recovery of energy from waste products in an economical and environmentally acceptable way.
9) Many business and executive management positions, especially in chemical- and material-based companies (both large and start-up), are filled by chemical engineers. This may come from the advancement over time of newly hired engineers based on demonstrated capabilities (including technical, decision making, and people interaction and motivational skills), as well as the need to transfer chemical engineers with one area of management and technical expertise into another needing, but not having those skills.
10) The study of biological systems from a chemical engineering standpoint. This includes not only the previously mentioned human organs such as the heart (pumps) and kidneys (filters) but also absorption and conversion of food ingredients into the human body.
11) Development of System Models. As our basic understanding of chemical and engineering systems has advanced, it has become easier to mathematically model many process systems. This requires the combination of chemical engineering skills with knowledge of mathematical models and software that, in many cases, minimizes the cost of system scale-up and evaluation.

Topics to Be Covered

The remainder of this book will be divided into chapters represented by the various chemical engineering unit operations, following an overview of safety, reactive chemicals, chemistry scale-up, and economics. The following general introductory topics will be included as necessary as each major chemical engineering unit operation is reviewed:

Chapter 2: Safety and Health: The Role and Responsibilities in Chemical Engineering Practice. There is no perfectly safe chemical (people drown in room temperature water). What particular aspects of safety are important in chemical processing and engineering? What are some examples of materials available and used to evaluate hazards and plan for emergency situations? What kind of protective equipment may be required? What particular aspects of chemical safety require special planning and communication? What are some examples of public- and government-required information? How do we decide on necessary protective equipment? In most cases of commercial processes, there is a wealth of safety and health information available, but discipline is required to review and keep up to date with the latest information. The stability of chemical systems to temperature and heat, oxygen, classes of chemicals, and external contamination must also be understood.

Chapter 3: The Concept of Balances. One of the core principles in chemical engineering is the concept of conservation principles. The amount of mass entering a process or a system, over some period of time, must be equal to what comes out. The same is true for energy with the addition or subtraction of energy change in any chemical reaction and also energy related to equipment operation such as pumps and agitators. Momentum, or fluid energy, is another property conserved in any process.

Chapter 4: Stoichiometry, Thermodynamics, Kinetics, Equilibrium, and Reaction Engineering. How a chemical reaction system, a separation system, a mixing system, a fluid transfer system, or a solids handling system is "scaled up" from their laboratory origins is one of the keys to a commercially successful chemical or materials operation. The methods for doing this are, in most cases, not linear extrapolations. If the scale-up of a chemical process involves many different unit operations, whose scale-up methods are different, this presents a unique challenge in the design of a large-scale chemical process. Chemical reactions either require or generate heat. As will be discussed in more detail later, the rates of reactions and the ability to add and remove heat do not follow the same type of mathematical laws, requiring intelligent engineering design decisions to prevent accidents, injuries, and loss of equipment. Many chemicals will not react with each other under ambient conditions, but their potential products are desirable. Catalysts are materials with special surface properties, which, when activated in a particular way, allow chemicals to react at lower temperature or pressure conditions than otherwise required. They also may allow a higher degree of selectivity of products produced.

Chapter 5: Flow Sheets, Diagrams, and Materials of Construction. As a chemical process idea moves from a laboratory concept to full-scale production, it typically moves through various stages. A mini-plant, a small-scale version of the lab process, might be run to test variables such as catalyst life, conversions and yields being steady over time, reproducibility of the product produced, and similar issues. A pilot plant might then be built, which might be a 100× scale of the lab process, but still 1/10th or 100th the size of the full-scale plant. If it is necessary to provide product samples to a customer during this scale-up process, a semi-plant might be built. The prime function of such a unit is to supply product for customer evaluation, but it will certainly provide additional scale-up and design information. A process being scaled up by a company that is already familiar with the general chemistry may skip one or more of these steps, considering the scale-up risk to be minimal. As this scale-up process moves along, flow sheets that describe how the process will operate and how its various process units will interact with each other become more detailed.

An industrial process rarely uses the same type of equipment used in the laboratory, and one of the key differences is in the materials used in the equipment that handles all the process materials. On a large scale, it is neither safe nor practical to use large-scale glass equipment. Glass-lined equipment is an alternative but can be expensive. Decisions on materials of construction are part of this process of scaling up a process. Decisions on materials to be used must be made and involves corrosion rates and products of corrosion, as well as balancing corrosion rates and product contamination with the possible added cost of corrosion-resistant materials.

Chapter 6: Economics and Chemical Engineering. No chemical reaction or process is commercially implemented unless it provides a profit to someone. Many chemical reactions and formulations are proposed that never go beyond laboratory scale. There must be a demand for the material and the function it provides, and the value (price) of the product or service must be greater than the sum of the cost of its raw materials, the cost of the plant to produce the final product, the cost of any necessary and required environmental controls, the cost of final plant site cleanup and/or disposal, the cost of any borrowed funds invested, the cost of research and development related to the product and process, and the profitability demanded by a company and its shareholders. There may also be unique costs involved in the transportation and storage of any particular chemical.

As previously mentioned, the costs and quality of commercially available raw materials will differ significantly from laboratory reagents. In every case, if the quality will be lower, the raw materials will have impurities that are different, the levels of impurities may change with time, and costs of energy systems may vary. Since the construction of a commercial chemical operation may take many years to complete and the science of forecasting all of these variables is never perfect, estimates are made of changes in these inputs and how they would ultimately affect the cost of manufacture. Economics of making a material is also divided into components that are either fixed or variable, meaning that the costs vary directly with the production volume or they are relatively independent of the volume. The ratio of these two characteristics can have a dramatic impact on chemical or material process profitability as a function of volume and business conditions.

Chapter 7: Fluid Flow, Pumps, and Liquid Handling and Gas Handling. This chapter will review the basics of fluid flow including pumps, gas flow, piping systems, and the impact of changes in process conditions. Fluid transport equipment have limitations that must be understood prior to their choice and use. Fluid mixing can affect chemical reaction rates, uniformity of products produced, and energy costs used by various transport systems. Similar to mass and energy balances, fluid energy and momentum are also conserved in any fluid system, and these potential changes must be accounted for.

Chapter 8: Heat Transfer and Heat Exchangers. Since very few chemical reactions are energy neutral, heat must be either supplied or removed. There are many choices in heat transfer equipment as well as choices in how these various types of equipment are configured. Heat transfer systems are used to heat or cool the reaction systems, insulate piping to maintain a given temperature, maintain temperatures in storage systems, condense gases, boil liquids, and melt or freeze solids. The heating or cooling may also be used to control or change physical properties of a liquid or a gas. It may also be possible to use heat generated in one part of a process to utilize in another part of a process.

Chapter 9: Reactive Chemicals Concepts. This chapter, though separate due to its importance, combines aspects of kinetics, reaction engineering, and heat transfer in the analysis of what is commonly known as reactive chemicals. These aspects of engineering scale in the same way and, if not done correctly, can result in serious loss of life and equipment.

Chapter 10: Distillation. This is the most unique unit operation to chemical engineering. Many liquid mixtures, frequently produced from a chemical reaction, must be separated to recover and possibly purify one or more of the components. If there is vapor pressure or volatility difference between the components, the vaporization and condensation of this mixture done multiple times can produce pure products, both of the more volatile and less volatile components. This unit operation is at the heart of the oil and petrochemical industry that produces gasoline, jet fuel, heating oil, and feedstocks for polymer processes. Low temperature (cryogenic) distillation is also the basis for separating ambient air into its individual components of nitrogen, oxygen, and argon—all used in industrial and medical applications.

Chapter 11: Other Separation Processes: Absorption, Stripping, Adsorption, Chromatography, Membranes. Absorption is the unit operation that describes the removal or recovery of a component from a gas stream into a liquid stream. Stripping is the opposite, or the removal or recovery of a component from a liquid into a gas. Both of these unit operations have become more important over time as environmental regulations have decreased the amount of trace materials that can be discharged directly into the air or water. Adsorption is the use of gas/solid interaction to recover a component from a gas or liquid on to the surface of a solid, the fluid discharged, and the material on the solid surface later recovered via a change in pressure or temperature. The principles of adsorption can also be used to optimize the design of catalyst systems mentioned previously. Charcoal "filters" used to purify home drinking water are an example of this unit operation. Ion-exchange resins are often used to "soften" water for home and industrial use.

Some mixtures require more advanced separation techniques. Water desalination is such an example. Due to basic thermodynamic properties, water would prefer to contain salt, if it is present, rather than to be in its pure state. It is necessary to overcome this "natural" state through the use of permeable selective membranes utilizing a pressure differential. This can be a less costly way of producing drinking water from salt water compared to evaporation. Separation of gases (i.e., air into nitrogen and oxygen) into their components can also be done via membrane-based technologies versus cryogenic (below room temperature) distillation.

Chapter 12: Evaporation and Crystallization. Many chemical reactions result in a product dissolved in a process solvent. This can include salts dissolved in water systems. These types of solutions frequently require concentration to deliver a desired product specification or may require removal of a component whose solubility is lesser than the desire product. Heating or cooling such a solution can be used to evaporate or crystallize the solution and change its concentration of the dissolved solid. This unit operation and its principles overlap with heat transfer topic in Chapter 8.

Chapter 13: Liquid–Solids Separation. Filtration is basically the removal of solids from slurry for the purpose of recovering a solid (possibly produced via evaporation or crystallization). The purpose here could be either recovery of a valuable product, now precipitated, or further processing of a more pure liquid. A drip coffee maker is an example of filtration. This unit operation can be enhanced by the use of gravitational forces such as used in a centrifuge. A home washing machine in its spin cycle is an example of this unit operation.

Chapter 14: Drying. Many chemical products, in their final form, are solids as opposed to liquids or gases. The drying of solids (removal of water or a solvent from a filtration process) involves the contacting of the wet solid with heat in some form (direct contact, indirect contact) to remove the residual water or solvent. The degree of dryness needed is a critical factor in engineering design. The setting used in home clothes dryer is an everyday example.

Chapter 15: Solids Handling. The fundamentals of solids handling and storage are seldom included in chemical engineering curricula at the present time. However, the variables that determine how solids transport equipment (screw conveyors, pneumatic conveyors) operate are extremely important from a practical and industrial standpoint. The characteristics of solids and their ability to be transported and stored are far more complicated than liquids and gases and require the determination of additional physical properties to properly design such process units as bins and hoppers, screw conveyors, pneumatic conveyors, and cyclones. There are also some very unique safety concerns in solids handling, often ignored, that result in dust explosions. The caking of solids in a home kitchen storage unit is an everyday example of what can also happen in industrial processes and packaging.

Chapter 16: Tanks, Vessels, and Special Reaction Systems. Though the actual detailed design of structural supports, pressure vessels, and tanks is normally done by mechanical and civil engineers, the design requirements are often set by chemical engineers. Though tanks and vessels can be used to simply store materials for inventory or batch quality control reasons, they are also used as reactors. This can frequently involve mixing of liquids, gases, and solids; heat transfer; as well as pressure, phase, and volume changes.

Chapter 17: Chemical Engineering in Polymer Manufacture and Processing. These are materials produced from the reaction of monomers such as ethylene, styrene, propylene, and butadiene, which have reactive double bonds. When activated by thermal, chemical, or electromagnetic fields, these monomers can react among themselves to produce long chains of very high molecular weight polymers. Different monomers can be reacted together, producing co- and tri-polymers with varying geometrical configurations. This class of materials has both unique processing and handling challenges due to unusual physical properties and the nonuniform distribution of chemical characteristics. They also have unique challenges in blending and compounding to produce final desired product properties such as color and melting characteristics.

Chapter 18: Process Control. All of the unit operations and their integration into a chemical process require the design of a control system that will produce the product desired by the customer. This chapter also covers the aspects of a control system necessary to deal with the safety and reactive chemical issues mentioned previously.

Chapter 19: Beer Brewing Revisited. In follow-up to the first exercise, we will review the brewing of coffee from the standpoint of chemical engineering principles.

There are also appendices to provide additional discussion and reference materials.

Before we start our journey into the various aspects of chemical engineering, let us take a look at the flow sheet showing how beer is manufactured:

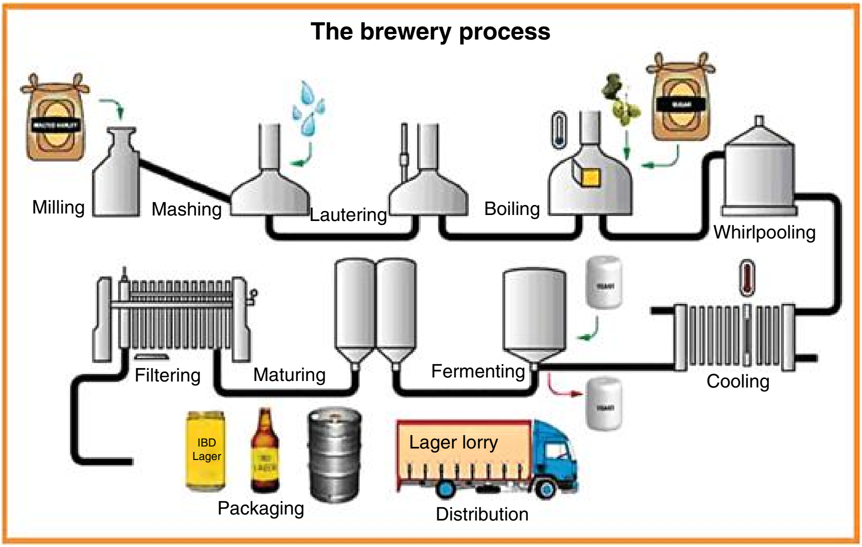

Figure 1.1 Beer manufacturing flow sheet. Source: https://chem409.wikispaces.com/brewing+process. © Wikipedia.

Prior to reading the rest of this book, make a list of some of the chemical engineering issues that you see in designing, running, controlling, and optimizing the brewery process.

1) ______________________________
2) ______________________________
3) ______________________________
4) ______________________________
5) ______________________________
6) ______________________________
7) ______________________________
8) ______________________________

We will revisit this process near the end of this book.

In addition we will use the brewing of coffee (starting at the very beginning) as an illustration of the principles we will present throughout the book.

Discussion Questions

1 What roles do chemical engineers fill in your operations and organization?

2 What unit operations are practiced in your process and facility? Which ones are well understood? Not well understood?

3 How are nonchemical engineers educated prior to their involvement in chemical process operations? Have there been any consequences due to lack of understanding of chemical engineering principles?

4 What chemical process operations are used in your process? How is the knowledge about these unit operations kept up to date? Who is responsible?

5 What areas in your organization's future plans may involve chemical engineering?

Review Questions (Answers in Appendix with Explanations)

1 Chemical engineering is a blend of:
A __Lab work and textbook study of chemicals
B __Chemistry, math, and mechanical engineering
C __Chemical reaction mechanisms and equipment reliability
D __Computers and equipment to make industrial chemicals

2 Major differences between chemistry and chemical engineering include:
A __Consequences of safety and quality mistakes
B __Sophistication of process control
C __Environmental control and documentation
D __Dealing with impact of external variables
E __All of the above

3 A practical issue in large-scale chemical operations not normally seen in shorter-term lab operations is:
A __Personnel turnover
B __Personnel protective equipment requirement
C __Corrosion
D __Size of offices for engineers versus chemists

4 Issues that complicate large-scale daily chemical plant operations to a much greater degree than laboratory operations include all but which of the following:

A __Weather conditions

B __Emergency shutdown and loss of utility consequences

C __Upstream and/or downstream process interactions

D __Price of company, suppliers, and customer stocks that change minute by minute

5 A chemical engineering unit operation is one *primarily* concerned with:

A __A chemical operation using single-unit binary instructions

B __Physical changes within a chemical process system

C __Operations that perform at the same pace

D __An operation that does one thing at a time

Additional Resources

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2

Safety and Health

The Role and Responsibilities in Chemical Engineering Practice

Basic Health and Safety Information: The Material Safety Data Sheet (MSDS)

We often hear the term "hazardous chemicals" as if this were different from other normal materials. We sometimes describe water as if it is not a chemical, but it is! It has a chemical formula (H_2O), and thousands of people die in it every year (by drowning or being carried away in floods) at room temperature, yet we cannot live without it for more than a few days. Every material has a chemical formula and every material, under some conditions, can cause harm. People are also thermally burned by steam. Gasoline, in conjunction with an internal combustion engine, is a necessary material to move a car, but this same material is highly flammable (but only under certain conditions) and can burn cars to the ground and cause serious burns to a car's passengers, or can be used in arson. It is a chemical engineer's (along with chemists, toxicologists, and biologists) job to clearly define what these hazardous conditions might be and how they might be created and then not only to prevent these situations from occurring but also to communicate clearly to those around us and who work with these materials this same information and the best known ways of dealing with an unsafe situation. For example, what is the best way to put out a gasoline fire? How can it be prevented?

The basic set of information that should be available for any chemical or material includes this information. This listing follows the outline of a particular compound's Material Safety Data Sheet. This is a summary document required to be supplied to a customer of any supplier. A web reference to view an MSDS sheets is included in Appendix II. Very recently, the US Occupational Health and Administration (OSHA) has changed the description of these sheets to simple "SDS," meaning Safety Data Sheets, standardizing on a 15 subtopic format. The link to OSHA's new SDS outline is included in the references at the end of this chapter.

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1) The Name, Chemical Formula, and Supplier of the Compound. Since some chemicals have "nicknames," which may not give a clear indication of what the material is, this is absolutely essential. The word "water" tells us nothing about what its chemical formula is (though most of us know it from strictly convention and habit), and we could legally describe it as dihydrogen oxide instead of the familiar chemical term "H-2-O." This may seem like a trivial example, but the word "octane" when we hear in conjunction with gasoline can imply several different chemical compounds, all of which contain 8 carbon atoms and 18 hydrogen atoms. There are several different ways of arranging these molecules, and without being specific about the physical arrangement of them (linear? branched? in what way?), we may design an improper fire protection system, supply the wrong octane gasoline, or miscalculate its boiling or freeing point. It might be assumed that any chemical would have the same information regardless of who supplied it, but that is a dangerous assumption. Different suppliers may have different levels of impurities, especially if the same material is produced via a different process, a fairly common situation in the chemical industry. Different suppliers may also have different levels of knowledge about a material they supply.
2) The General (Not Specific) Nature of the Hazards of the Material. Is it particularly toxic? In what form? Is it flammable? Over what range of concentration in air? How easy is it to ignite the material? Are there special hazards to be aware of? Is it water reactive? Is it a strong oxidizer?
3) The Compound's Chemical Composition. As mentioned previously, this needs not only the chemical constituents but also an accurate description of the chemical configuration (more on this later when we discuss geometrical and optical isomers), as well as impurities typically present, to what degree and over what ranges. There is no such thing as a pure material. The impurity level could be at the microscopic level (e.g., PPM) or in the several percent level. As mentioned in #1 earlier, the process to manufacture a chemical could affect the general nature of the impurities.
4) First Aid Measures. If individuals who are involved in the manufacture, distribution, or use of the material were to be exposed to it, what needs to be done? For how long? What do emergency responders need to know? What do emergency room physicians need to know? What special counteractive measures need to be immediately available? To whom? What are the different measures required to deal with inhalation, skin exposure, and oral ingestion? Should vomiting be induced? (You might ask yourself why this is important.) Why or why not? What should be done in the case of accidental spills or releases? What kinds of neutralization or countermeasures need to be immediately available? What kind of protective equipment is needed to handle the material? Gloves, goggles, rubber suits, respiratory masks? Special eye, skin, and respiratory protection? Any special areas of concerns, such as rapid skin absorption or desensitizing olfactory nerves?

5) Fire Hazard and Firefighting Concerns. If the material is totally nonflammable, there would be nothing listed here (in fact "nonflammable" should be clearly stated), but if a material's decomposition under heat or fire could produce flammable or toxic by-products, this would be listed. If a material is flammable, what is its flammability range (the same information reported previously)? What energy levels are required to ignite a material within its flammable range? Does the flammability range change with pressure? There are some materials where water is not the preferred means of extinguishing. For example, a flammable, water-insoluble material may be spread out and make the situation worse. A material may be water reactive. What is the alternative, preferred measure? Is the local fire department aware of this? Do they have the alternative materials (e.g., carbon dioxide) on hand at all times? Are drills held that collaborate with the local emergency responders?
6) Accidental Releases and Spills. What should be done? What kind of emergency prepared response is required? By whom? If a spill could result in a discharge to a water source that is also a municipal drinking water supply, what emergency procedures are in place? Is there frequent and up-to-date communication with municipal authorities and emergency responders? Are there conditions under which corrosion of piping or storage systems could be accelerated? If so, how are they monitored?
7) Handling and Storage. What kind of material should be used to store or transfer the material? Are there special corrosion issues? For example, compounds containing chloride or which may produce chloride ions in a reaction should not be handled in stainless steel. Normal carbon steel may be appropriate. Chloride ions can interact with grain boundaries in stainless steel to produce catastrophic failure, as opposed to just accelerated corrosion. A more expensive material cannot be assumed to be more corrosion resistant. A classic example of this is chlorine's interaction with carbon steel as opposed to the more exotic metal titanium. If chorine is very dry, it can be normally handled in carbon steel; if wet, however, it will aggressively attack steel and rapidly corrode it. Wet chlorine will not attack titanium piping, whereas dry chlorine will react with titanium immediately to form titanium tetrachloride, a reaction that resembles a fire. It is *never* safe to rely on gut feelings to choose materials for storage and piping.
8) Exposure and Personal Protection. We need to know what kind of personal protective equipment (frequently referred to as PPE) is required to be worn by those who handle a given material. If a skin burn or irritation is possible, what kind of PPE is mandated? Gloves? Safety suits? What kind? Made of what material? How often should it be inspected or replaced? Are the potential hazards of materials and the required protection adequately communicated?
9) Physical Properties. All chemicals have defined melting and boiling points, but these can be affected by the presence of impurities. Some materials,

when they melt, can change from a white solid to a colorless liquid, negating the visual sign of the presence of the chemical. Boiling points will vary with pressure. Many times, the boiling point of a material is assumed (from its ambient pressure information) and then not recalculated for a change in pressure, thus allowing vapor escape under conditions not considered.

10) Stability and Reactivity. Many chemicals and materials are stable (meaning that they do not decompose to any measurable degree when stored or used). Others can decompose, to varying degrees, as a function of temperature or in combination with other materials. For example, acids and bases will react with the release of energy. The chemical system that allows a car air bag to protect us (sodium azide) is a chemical that decomposes under shock to generate nitrogen gas which, when released, causes the inflation of the air bags. In this case, we use the known instability for a useful purpose, but obviously, if this reaction occurred without awareness of its occurrence, a major safety incident could result. The type of materials used to contain and transport chemicals is also under this classification. The types of metals and their corrosion rates, as a function of temperature and impurities, need to be known. We previously discussed the unique nature of chlorine systems. The point is that decisions on materials, corrosion, and storage need to be based on data and not assumptions.
11) Toxicology Effects. Different classes of compounds can concentrate in different body organs. For example, halogenated organic compounds tend to concentrate in the liver. Caustic compounds and bases can seriously impact the eyes and skin. It is important to know the toxicological effects of the materials to individuals who handle or may come in contact with the material of concern. This information also needs to be shared with customers and included in an MSDS or SDS sheet supplied to them. This information needs to cover impact and interaction with the skin, eyes, and internal organs such as the lungs and liver. It also usually includes information known to impact unborn children, reproductive organs, and cancer causation.
12) Ecological Information. If released to the environment, how does the material bio-concentrate? In what species? Does it concentrate in sediment? A compound's solubility in water will play an important role in this. How does the compound biodegrade? By what mechanism? What information is required to be supplied to environmental agencies? If a material is released, what is the effect on drinking water supplies?
13) Disposal Information. In laboratory situations, small quantities of chemical wastes may be simply put into special waste containers, and a commercial disposal company removes it. On a larger scale, these types of materials come under a large number of regulatory requirements, which may also

depend on the state in which the operation is being conducted. These requirements must be rigidly adhered to. In some large chemical complexes, there may be ways of recycling or reusing the material. It is also possible to incinerate the material, via combustion or pyrolysis, to generate reusable heat or starting raw materials.

14) Transport Regulations. Many chemicals are strictly regulated by the Department of Transportation (DOT) that regulates how chemicals must be stored, shipped, and labeled. In addition, individual states may have additional labeling and informational requirements. It is critical that chemical engineers, especially those involved in manufacturing and distribution, understand the most up-to-date versions of these regulations.
15) Other Regulatory Information. Information such as “right to know” laws, SARA 313 classifications, MSDS updates, RECRA, etc. are necessary for chemical engineers handling materials to be aware of and ensure compliance. This can be especially important if someone changes geographic locations where the state requirements may be different. There can also be National Fire Protection Association (NFPA) information that must be updated to ensure that DOT shipping labels used to assist emergency responders are up to date.

It is extremely important to keep up to date on MSDS sheets. Though it can become a habit to throw away the latest one received since there are many files already, it is critical to review the latest MSDS sheet and replace older ones with out-of-date information.

Procedures

In addition to basic knowledge of the chemical’s properties, it is critical, when handing or processing chemicals, that recognized standard procedures, processes, and safety requirements specified for their use and handling are followed. These are usually above and beyond of what may be included in an MSDS sheet as the way chemicals and materials are handled and processed will vary greatly from company to company and from site to site.

This aspect of chemical handling includes special circumstances such as start-ups, shutdowns, and emergency shutdowns. These procedures are always different than those used in a steady-state operation, and it is difficult to consider all possibilities, requiring awareness and the ability to react to unusual and unanticipated conditions. These can include leaks from tanks and piping, transportation emergencies, emergency reactions to external situations from weather or emergency situations from upstream or downstream processes, loss of utility supplies, and other unanticipated situations.

Fire and Flammability

A particular concern in the chemical and petrochemical industries is handling flammable materials. We are generally familiar with such materials as natural gas, gasoline, butane, propane, and acetylene, but there are many more materials that have potential flammability and explosivity issues. How do we characterize this type of hazard?

Materials that are flammable are not flammable under all conditions. In addition to the chemical (the fuel) itself, two other ingredients are necessary. The first is oxygen. The air in our atmosphere contains approximately 21% by volume oxygen, so oxygen is all around us. Flammable materials require a certain amount of oxygen to burn, but most of the time this level is below 21%, requiring padding with a gas such as nitrogen or argon. The second requirement is heat or an ignition source. The spark plug in our car provides this ignition source in our automobile, igniting a mixture of gasoline and air in certain proportions. This requirement for these three ingredients—fuel, oxygen, and heat/ignition—completes what we know as the fire triangle:

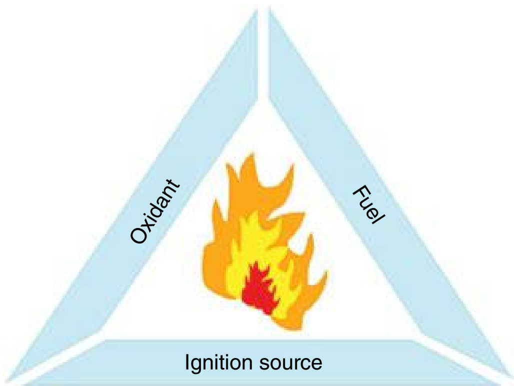

Figure 2.1 The fire triangle. Source: Chemical Engineering Progress, 4/12, pp. 28–33. Reproduced with permission of American Institute of Chemical Engineers.

There are many different color conventions used in this diagram, but the fuel will always be at the bottom of the triangle, the ignition or heat source on the right side of the triangle, and the oxidant on the left side of the triangle. Without all three of these ingredients, it is not possible to sustain a fire. In the context of this diagram, heat is often the by-product of an ignition source. It is also important to remember that an "oxidant" can be something other than oxygen (O_2). Strong oxidizing materials such as peroxides, chlorates, bromates, and iodates can also supply the oxidant function needed. It is easy to assume that the simplest way to prevent a fire is to simply remove heat and ignition sources. While it may be possible to eliminate high temperature sources of heat, it is nearly impossible to eliminate ignition sources. Friction generates heat and is all around us. It is generated by moving machinery parts such as shafts and bearings, friction caused by someone simply walking across a nonconductive surface (as illustrated by the static charge you feel when shaking hands with someone after walking across a carpet in the winter time with low humidity), by something as simple as a fluid flowing through a plastic, non-conductive pipe, or by liquid being sprayed into an open tank. Fires have been caused at traditional gasoline filling stations via the buildup of static filling a plastic versus grounded metal gasoline container. The only proven way of preventing fire is to eliminate the presence of oxygen. This is typically accomplished through the use of inert pad gases such as nitrogen.

We further characterize flammability by what is known as the lower and upper explosive limits (expressed as LEL and UEL, respectively). As flammable as gasoline may be, it is only ignitable and able to sustain a fire within certain limits of oxygen concentrations. At the lower limit, there is too low a fuel/oxygen ratio to sustain a fire. It may be possible to ignite a fire, but the fire cannot be sustained. Blowing out a birthday candle on a cake is an analogous situation as we provide so much air (oxygen) that the fuel/air ratio is too low and the fire goes out. At the other extreme, we can have a situation where the fuel/oxygen ratio is too high and there is not enough oxygen to react with the fuel. The failure of starting a lawn mower engine due to flooding is analogous to this. There is another important property of flammable liquids and that is their autoignition temperature. This is the temperature at which an external ignition source is not necessarily required to initiate combustion. At this elevated temperature, the system has enough thermal energy to act as an ignition source.

LELs and UELs are also affected by pressure and temperature, so measurements of this data must be over the actual planned process conditions. An increase in oxygen concentration, as well as a pressure increase beyond normal atmospheric conditions, can increase the range of flammability.

Minimum ignition energy (MIE) is the amount of energy required to ignite a flammable mixture. This value can vary significantly. For example, the MIE for acetylene is 0.02 mJ, while that for hexane is 0.248 mJ. This makes acetylene far more susceptible to ignition than hexane, but both are extremely flammable. Though ammonia is often considered to be nonflammable, it does have a flammability range between 16 and 25% oxygen. However, ammonia's MIE, is approximately 650 mJ. Though this is several orders of magnitude higher than the more flammable materials and is difficult to ignite, it is NOT nonflammable.

There are two important points about this kind of data. First, it is determined at a given pressure (the information mentioned earlier is at atmospheric pressure). The actual data for the pressure being used in the storage or in the process must be used. Second, the consequences of a fire or explosion are more severe in the middle of the LEL/UEL range. Explosion pressures typically reach their peak in the middle of this range, as shown in Figure 2.2, requiring explosion relief devices to be designed to handle the maximum pressure possible.

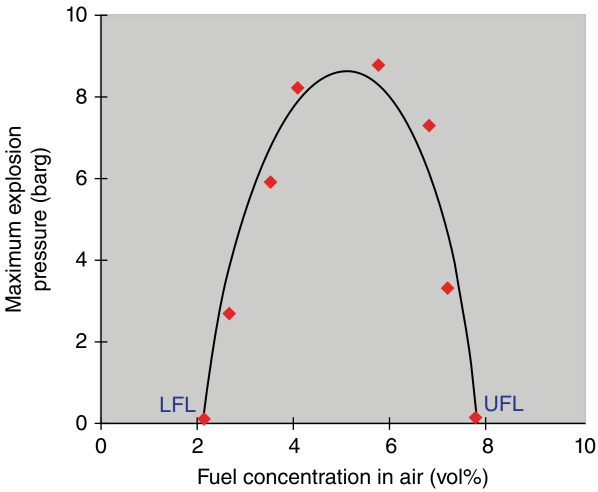

Figure 2.2 Explosion pressure versus fuel concentration. Source: Chemical Engineering Progress, 2/09, pp. 25–29. Reproduced with permission of American Institute of Chemical Engineers.

As with other data of this type, actual laboratory data should be used when available. An additional practical point is that the rate of pressure and energy increase with an explosion. Again, this is a parameter determined experimentally and is important in sizing relief systems. Each flammable material will have its own response curve. It is also important not to mathematically average individual compound data to estimate the explosion pressure for a system but to measure the data for the system as it exists in practice.

We classify explosions into several general categories. Deflagrations are fires and explosions where the propagation of the flame front is less than the velocity of sound (fire or explosion is seen before it is heard). Second, there are detonations, where the propagation of the flame front is less than the velocity of sound (fire or explosion is heard before being seen). "Explosions" describe the rupture of enclosed equipment or piping in an uncontrolled fashion. Fires and explosions can be caused by gases, liquids, or solids and we often ignore the latter. Some of the most deadly fires and explosions have been in the agricultural area with such materials as flour, sugar, and nitrate fertilizers and also in the traditional chemical industry with materials such as plastic dusts that have the capability to build up static charge. The special fire and flammability hazards of solids will be discussed in Chapter 15.

Chemical Reactivity

Classes of reactive chemicals that must be considered in this area for special attention include peroxides, monomers that self-polymerize, oxidizing/reducing combinations, and shock-sensitive materials. In addition, process operations that are heat generating need to be analyzed for their potential to generate sufficient energy to trigger a reactive chemical event. These include mixing and agitation as well as materials of construction that can react with process materials. Another area for review is the handling of inhibited monomers to prevent polymerization during storage and transport.

Special analytical tests, using a technique known as accelerated rate calorimetry (ARC), have been developed for analysis of reactive chemical systems. In these tests a system including the chemicals and materials of concern are slowly heated against a reference standard, and the point at which the reaction or decomposition rate exceeds the system's capability to remove the heat is clearly identified. The video in Appendix II explains the equipment used to determine this information in more detail.

We will discuss the broader subject of reactive chemicals in Chapter 9.

Toxicology

Toxicology is the study of how materials interact with a biological system. Within the scope of this book, we are discussing the effect of chemicals with humans. For many years, the chemical industry has developed and used biological models, primarily based on animal testing, that allow the prediction of toxicological effects of chemicals on the human body as well as specific organs within the body. These tests have been done primarily through the use of mice and rabbits as models for chemical interaction with the human body. Though great progress has been made in identifying methods using cell cultures as an alternative, animal testing still remains the often used method of predicting human organ response to chemical exposure.

There are two general classifications of exposures that we must consider: acute and low level, sustained exposure. For example, the effect of a major spill of an acid, alkali, or toxic gas will be quite different than a slow sustained release of the same material over several years. The first will require a defined emergency response and immediate life-saving procedures, while the second will require constant monitoring and medical testing.

Human exposure to chemicals can occur via several routes, including eye, oral, skin, and lung exposure. A particular chemical may have special greater impact on a certain part of the body or organ, and protection specified against exposure will be affected by this impact. Protective equipment is specified based on our knowledge of these effects. Suppliers of chemicals provide this knowledge to their customers as part of chemical industries' efforts more commonly known as "product stewardship." This concept extends beyond the safe handling of chemicals to include transportation issues and waste disposal and treatment.

Emergency Response

Despite the best plans and intentions, emergency situations can occur due to loss of utilities, human error, and, unfortunately in today's world, terrorism. These types of incidents may occur at the local manufacturing site or thousands of miles away as a result of transportation accidents.

Dealing with emergencies requires preplanning, as well as practiced reaction and drills to unanticipated events. Preparedness for such events includes communication (to employees, emergency responders, and surrounding communities), ensuring that the local community and transportation providers have the most updated safety, toxicological, and medical information. Drills and preplanning are often done in conjunction with local emergency responders and medical facilities that may be called upon to treat victims of unanticipated releases or exposures. In many bulk commodity chemical areas such as chlorine, suppliers have banded together in a pact to allow the nearest manufacturer to respond to an emergency, as opposed to the original supplier having to travel thousands of miles and delay the necessary response.

Transportation Emergencies

When chemicals are transported by land, sea, or air, response to spills or leaks caused by accidents can be a major challenge to emergency response personnel, as they do not have the training or awareness of a local emergency response group close to a chemical facility. For this reason the NFPA, in collaboration with chemical industry, developed a visual diamond symbol for use on transportation vehicles, as seen in Figure 2.3.

Though this diamond typically does not tell the emergency responder the name of chemical formula, it does provide the following important information:

1) What is the nature of the health hazard? Is it relatively harmless or a highly toxic? This section of the diamond is typically shown in a dark gray color (left section of the diamond).
2) What is its flash point? This tells the emergency responders the degree they need to consider serious fire and explosion potential, including keeping spark-producing devices (such as cars) away. This section of the diamond, at the top, is typically a medium gray color.

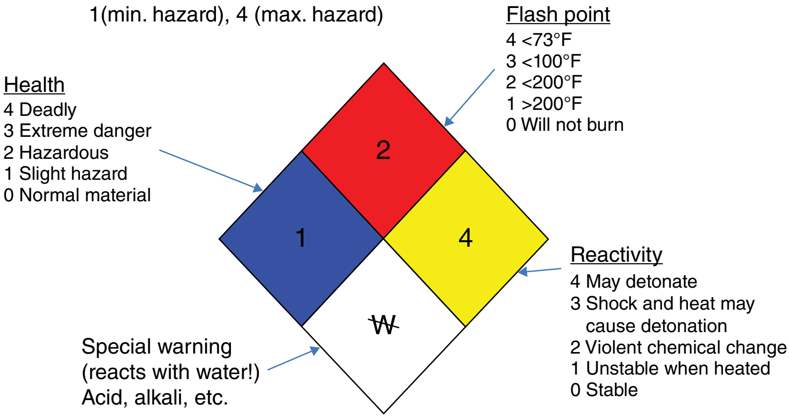

Figure 2.3 The NFPA diamond. Source: Reproduced with permission of U.S Department of Transportation.

3) How reactive is the material? Is it shock or heat sensitive? This section of the diamond is typically shown in a light gray color, in the right section of the diamond.
4) The white section of the diamond at the bottom may be blank, but it is the place where any special hazards can be indicated. In this particular case in Figure 2.3, this section shows that the material reacts with water, so the emergency responders might use carbon dioxide (CO_2) as the fire-extinguishing media, as opposed to water. Public emergency responders are generally well educated in this diamond as well as the meaning of the colors, numbers, and symbols within it.

HAZOP

As a result of a major incident at a petroleum depot in Flixborough, England, and others that followed, a formal review process was instituted within the chemical industry that is now known as hazard and operability study (HAZOP). This review process has become one of the bulwark review processes used in the chemical industry and takes a different form than a typical review where the specified flows, temperatures, pressures, and levels are reviewed, and the primary focus is on how to maintain and control the parameters within their specified limits.

In a HAZOP review, we do just the opposite. We ask, in a very systematic way, what happens if the parameters are NOT where they are designed to be.

For example, if a chemical reaction vessel is designed to operate at 100 psig and 200°C, we might ask the following types of questions:

1) What happens if the pressure is lower than 100 psig? Higher than 100 psig? How much higher or lower? For how long?
2) What happens if the reactor temperature is lower than 200°C? Higher than 200°C? How much lower or higher? For how long?

Are the consequences merely production of an off-spec product which may have to be recycled or disposed of? A release of a toxic material? Production of side products contaminating the primary product? Rupture of a vessel? Fire or explosion? Of what magnitude?

Obviously there are many more process variables in addition to temperature and pressure in a process. These would include rates of flow, direction of flow, lack of flow, compositions, sequence and rates of additions in batch processes, potential contamination of desired material flows, direction of flow, substitution of the wrong material, and many others.

We can easily envision a simple household example of this process thinking about our home showers and asking these types of questions, whose answers are straightforward and may depend on a particular situation, just as in a chemical plant:

1) The temperature of the hot water is supposed to be 120°F, controlled by a thermostat in a hot water tank. What if the water comes out of the tank at 140°F? 160°F? Thermal burns are seen typically at 140°F, so this control is critical. How many "backup" controls on the hot water heater are necessary? Desirable? Affordable? Most people using a shower blend the hot and cold water to give a desired temperature. Could 140–160°F water be produced if the supply of cold water is stopped? How could this happen? Does the hot water supply need to be automatically shut off if this happens? During a plumbing repair on a system, could the cold and hot water supplies to the valves be reversed? What happens if the heating unit fails? An uncomfortably cold shower or do the water lines freeze? If they freeze and burst, what are the consequences? To whom? Under what circumstances?
2) The pressure in the water system is controlled to a great degree by the public utility or a privately operated water well system. What if the pressure suddenly drops because of a water main break? Is this a major safety issue or just a major inconvenience? What if it rises unexpectedly? Could a pipe burst? Where would the leaking water go?
3) The plumbing system is normally designed to allow water to drain from the tub or shower. What happens if the drain clogs and the tub overflows? Where does the water go? Is there a difference between the impacts of such an event if the shower is on the 10th floor of a building versus the ground floor? How long does the water need to flow with a plugged drain to cause a problem?

4) Could something other than water get into the supply piping? If so, what could it be and how would it be detected? Can too much water softener cause an extremely slippery surface? Could backup involving waste water happen? How?

The key to these types of reviews is the discipline of asking all of the right questions about all aspects of a process and not to rely on random thought or brainstorming. Table 2.1 shows a list of typical questions used in a HAZOP review and an example of their meaning.

Table 2.1 Typical HAZOP questions.

NO (none of design intent achieved)	Flow is 0 versus 40 GPM design
MORE (more of, higher) quantitative increase in parameter	Flow is 60 versus 40 GPM design
LESS (less of, lower) a decrease in parameter	Flow is 20 versus 40 GPM design
AS WELL AS (an additional activity occurs)	Material is contaminated
PART OF (only part of the design intent is achieved)	40 GPM for 10 min versus design of 40 GPM for 20 min
REVERSE LOGICAL (opposite of design intent occurs)	40 GPM is pumped into a tank versus a design of 40 GPM leaving a tank
COMPLETE SUBSITUTION (vs. design intent)	40 GPM of chemical B versus the intended 40 GPM of chemical A
WHERE ELSE (vs. design intent)	Flow goes to tank A versus tank B
BEFORE/AFTER	In a batch sequence, A is added after B versus the design of A and then B
EARLY/LATE	A is added 15 min into the batch sequence versus 10 or 20 min
FASTER/SLOWER	A is added at 40 GPM 10 min into the batch sequence versus 30 GPM design intent
COUPLING	In addition to a flow error, timing sequence and/or direction of flow is also an error

Many industry accident case studies have taught us valuable lessons that can be applied in this area as well as safety in general:

1) Communication. In large organizations, it is possible for different groups of people to have different levels of knowledge about chemicals, which is not necessarily passed on to all those whose safety may be impacted. Examples include chemical decomposition temperatures, reactivity information, corrosion information, and effects of extreme temperature.
2) Material Stress. Chemical engineers, in general, are not deeply trained in materials science. We often forget that metals change volume with temperature.

This must be considered in the start-up and shutdown of process equipment, especially heat exchangers that may be using high temperature fluids and/or refrigerants. These types of equipment must have defined, orderly, gradual start-up and shutdown procedures to minimize the chances of tubes breaking from tube sheets or high pressure being unexpectedly created by blocking flow of a refrigerant that could evaporate and create pressure.

Layer of Protection Analysis (LOPA)

There is another widely used safety analysis system that can add to conventional checklists, which is the concept of "layers of protection." As a simple illustration, consider leaving your house for a trip. How you approach this analysis may depend on whether you are living alone or with someone you care about. It may also depend on where you live and the attention of your neighbors. Assuming you are worried about a possible intruder, your first "layer" is to lock the doors and set up possibly a motion detector around your house. Depending on your confidence in this first layer and whether your spouse is a sound sleeper, you might jam doors or windows in an attempt to cause a break-in to generate significant noise from glass shattering and arouse someone who is sleeping. If you don't consider this commotion enough to scare away an intruder, you could install a local alarm, triggered by the opening of doors or windows. Whether this alarm is actually hooked up to an emergency call to the local police may be irrelevant if the intruder thinks it is. The sound of the alarm may also alert neighbors who may investigate what is going on. Then of course that alarm can be connected to an actual central alarm station that will call the local police and in addition have a live movie camera attached, which will film the intrusion and provide additional evidence for the police. Now if your house is a mansion full of precious gems, you might add to all of these a hired guard, and just in case you're really worried, you can hire a backup guard.

Each of these layers cost additional money. How do you decide on how much money to spend? That depends. What is the likelihood of the event happening? What is the history of robberies and intrusions in your neighborhood? How soundly does your spouse sleep? How reliable are the various alarm companies and what do they charge? Is it allowable to have a hired gun in your subdivision? There is no one correct answer here, but each of us goes through this type of analysis, even though somewhat superficially, when we leave our house or when we leave our car unattended. Do we leave it open, saving a few minutes when we return? Do we leave the keys in the car? We make a mental calculation of the risk and what we are willing to spend to minimize or eliminate it. We can use this same approach in deciding what level of investment and the nature of that investment that will minimize the impact from a hazardous operation or potential release.

Let's consider the example of a tank containing a hazardous material, either because of its potential fire hazard or the toxicity of the material in the tank. At the start we may have some regulatory requirements to meet such as diking, vent control, and others depending on the nature of the chemical and the state or county in which the tank is located. But after this we have decisions to make. We need to know the level in the tank to ensure that it does not overfill. Is one level indicator enough? What does an additional one cost? What are the financial, environmental, and business implications of the tank overflowing? How reliable is the instrument itself? What is the reliability of the utilities that supply the energy to run it? Do we need a backup air or electricity supply? Is the tank a raw material supply to another part of the same complex? Another customer? Are the consequences the same? There are no right or wrong answers to any of these questions, but they must be consciously answered, and decisions must be made as to the cost of measurement, assessment, and reaction for each system we have concerns about. We also have to think seriously about all of the possible "initiating" events that might trigger a response and how often they might occur. These last two items can change with time and need to be revisited on a regular basis.

An LOPA for a process reactor can be seen in Figure 2.4. An initiating event (i.e., pipe leak, spark, incorrect recipe for a batch reaction, high pressure, or loss of electrical power) may trigger an "event." For example, a pipe leak can happen due to an overpressure or corrosion problem. In our initial design, we may have incorporated a leak detection system for such a possibility tied to a control system to shut off flow through this pipe (levels 2, 3, and 4). The second layer could very well duplicate instrumentation and shut off systems that are activated if the first two do not function. Is the pipe leak in a cooling water supply to an exothermic reactor which may, if cooling is lost, cause a runaway and release materials in an uncontrollable way? This layer may have embedded within it a way for each instrument to communicate with each other as to proper functioning. That may be adequate. Is a third layer necessary? It still depends. On what? How close is the operation to the surrounding residential area? The science of LOPA calculations can become quite complex, and software programs and training is available to assist in these efforts. It is worthwhile noting that the only way to never have a release of any sort is not to build a plant.

Summary

The safe handling of chemical and the safe operation of the plants that make them is a primary responsibility of a chemical engineer. Many informational, evaluation, and analytical tools have been developed over the years to ensure that we have the most appropriate tools and data we need to provide this assurance to the organizations and communities we work with.

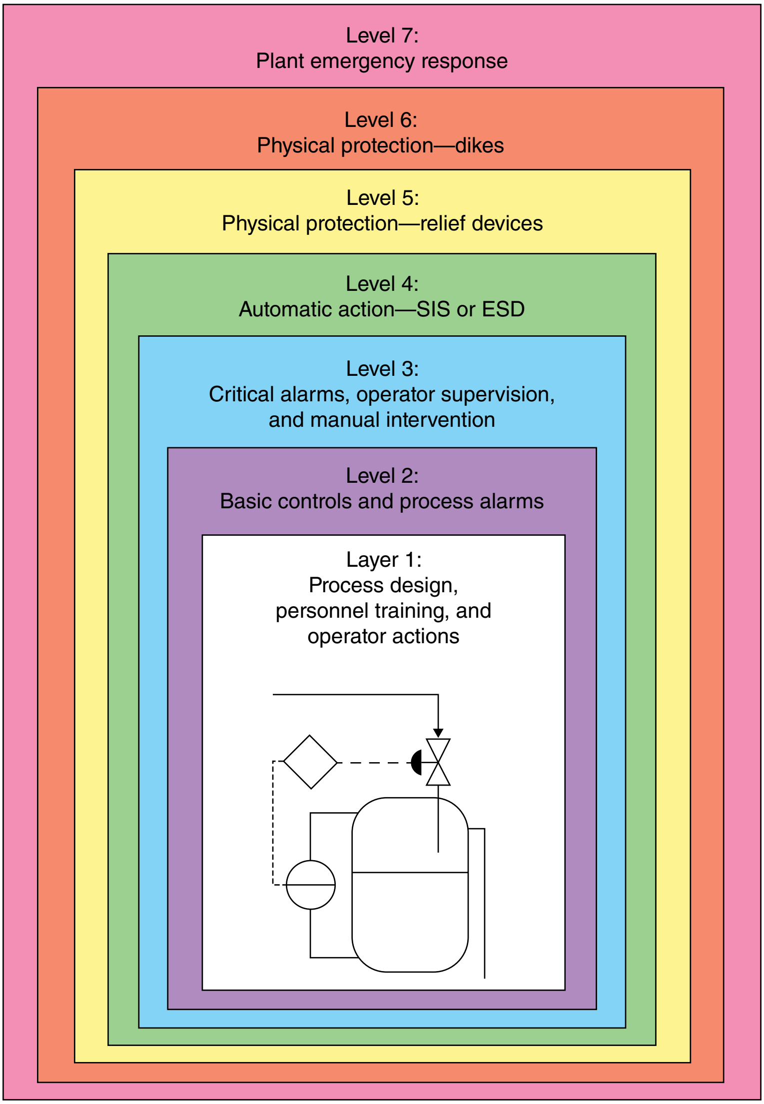

Figure 2.4 A layer of protection analysis. Source: Chemical Engineering Progress, 2/16, pp. 22–25. Reproduced with permission of American Institute of Chemical Engineers.

The American Institute of Chemical Engineers (AIChE) incorporates as part of its professional ethics statement, one which reads as follows:

> Engineers shall hold paramount the safety, health and welfare of the public in the performance of their duties

This is what everyone involved in chemical processing needs to remember and *never* lose sight of.

Coffee Brewing: Safety
What safety aspects are involved in this chemical process? Isn't it a chemical process? Does coffee sitting on a hot plate for several hours taste the same as when it first was dripped or perked? There is a chemical degradation reaction occurring. Whether we are brewing instant coffee or producing percolator or drip coffee, hot water is needed. Where does it come from? Depending on your preferences, you might use hot water from a spigot to add to instant coffee in a cup. This is usually not hot enough to produce a desirable beverage, so the water may come from an electrically heated water stream in the sink. Since water can scald (cause first degree burns above 140°F), we should ask how this setting is made. What can cause it to fail? Inject too much electrical heat into the water? Since we are using water around an electrically powered machine (coffee brewer or from a chemical engineering standpoint, a leaching process), can a short develop and possibly electrocute the user? We see ground fault interrupters (GFIs), usually required by building codes (safety rules and procedures), interrupt the supply of electrical current faster than anyone can do physically and, in most cases, prevent a shock or electrocution. We will learn more as we move further along in the course.

Discussion Questions

1 What kinds of fire, health, and environmental impacts are present in your processes? Is there a standard review process? How often is it done? Who attends? What is done with the information? Filed away or brought out for constant review?

2 After any incidents relating to fire, safety, health, or environmental discharges, what kind of reviews are done? Is it established why the normal protective processes did not work? If procedures were in place, why were they not followed? What kind of disciplinary or training changes are needed? Have there been any changes in the surrounding community that would warrant a revisiting of past practices?

3 Are the elements of the fire triangle well understood? Is the assumption of no ignition source being present a method of prevention? If inadequate oxygen is relied upon as the primary prevention mechanism, how is it checked? What could circumvent it? How many layers of protection are needed? How was the number of layers decided? What factors were considered in the cost/safety decisions?

4 Have all of the issues and variables in scaling up a lab process been considered? What is the next scale level that is appropriate? How much of the decision was economics versus technical risk? How was this balance decided? What factors were involved in the decision making?

5 Is flammability data for the actual chemical mixtures involved being used or mathematically averaging single comment data? Have the effects of pressure variation been considered? Do you have the actual data? If not, how do you plan to obtain it? When?

6 Are sensitive and reactive chemicals being handled? Are there proper storage and separation conditions? If refrigeration is needed, how many layers of protection are appropriate to ensure unsafe temperatures are not reached? Does the local fire department know how to handle such materials? Do they know what to do if asked for their help? Do they even know that such materials are used?

Review Questions (Answers in Appendix with Explanations)

1 Procedures and protective equipment requirements for handling chemicals include all but:
A __Expiration date on the shipping label
B __MSDS sheet information
C __Flammability and explosivity potential
D __Information on chemical interactions

2 Start-ups and shutdowns are the source of many safety and loss incidents due to:
A __Time pressures
B __Unanticipated operational and/or maintenance conditions
C __Lack of standard procedures for unusual situations
D __All of the above

3 The “fire triangle” describes the necessary elements required to have a fire or explosion. In addition to fuel and oxygen, what is the third item that must be present?
A __Ignition source
B __Lightning

C __Loud noise
D __Shock wave

4 The NFPA "diamond," normally attached to shipping containers, indicates all of the following except:
A __Degree of flammability hazard
B __Degree of health hazard
C __Name of chemical in the container
D __Degree of reactivity

5 The lower explosive limit (LEL) and upper explosive limit (UEL) tell us:
A __The range of flammability under some conditions
B __The range of flammability under all conditions
C __The upper and lower limits of the company's tolerance for losses
D __The upper and lower limits of the amount of flammable material pumped into a vessel

6 Autoignition temperature is the temperature at which:
A __The material loses its temper
B __A material automatically explodes
C __A material, within its explosive range, can ignite without an external ignition source
D __Fire and hazard insurance rates automatically increase

7 Toxicology studies tell us all but which of the following:
A __The difference between acute and long-term exposure effects
B __Repeated dose toxicity
C __Areas of most concern for exposure
D __To what degree they are required and how much they cost

8 An MSDS sheet tells us:
A __First aid measures
B __Physical characteristics
C __Chemical name and manufacturer or distributor
D __All of the above

9 A HAZOP review asks all of these types of questions except:
A __Consequences of operating outside design conditions
B __What happens to the engineer who makes a bad design assumption
C __Safety impact of operating above design pressure conditions
D __Environmental impact of discharge of material not intended

Additional Resources

Crowl, D. (2012) “Minimize the Risk of Flammable Materials” *Chemical Engineering Progress*, 4, pp. 28–33.

Fuller, B. (2009) “Managing Transportation Safety and Security Risks” *Chemical Engineering Progress*, 2, pp. 25–29.

Goddard, K. (2007) “Use LOPA to Determine Protective System Requirements” *Chemical Engineering Progress*, 2, pp. 47–51.

Grabinski, C. (2015) “Toxicology 101” *Chemical Engineering Progress*, 11, pp. 31–36.

Karthikeyan, B. (2015) “Moving Process Safety into the Board Room” *Chemical Engineering Progress*, 9, pp. 42–45.

Wahid, A. (2016) “Predicting Incidents with Process Safety Performance Indicators” *Chemical Engineering Progress*, 2, pp. 22–25.

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www.nfpa.org (accessed August 30, 2016).

www.nist.gov/fire/fire_behavior.cfm (accessed August 30, 2016).

https://www.osha.gov/Publications/OSHA3514.html (accessed August 30, 2016).

3

The Concept of Balances

Let's explore this general concept in more detail as it underlies so much of fundamental chemical engineering analysis, thinking, and problem solving.

Mass Balance Concepts

Assuming that we have the appropriate understanding of the fundamentals of our reaction and the physical properties of our materials, we can begin to think about the design of a process to manufacture the materials of interest. There are two fundamental concepts that must be understood and taken into account into the design and operation of any process. First, mass must be conserved. Put another way, what comes out of a process must be what we put into it *plus* whatever mass is accumulating within a system.

Chemical Engineering Progress and the Beacon publication from AIChE's Center for Chemical Process Safety have reported many cases of major fire and environmental disasters via the simple mechanism of overflowing tanks. The most significant of these was the Flixborough disaster, summarized in a *Chemical Engineering Progress* "Beacon" article (9/2006, p. 17). Faulty instrumentation, an inadequate number of layers of protection, and insufficient communication have all been causes of major environmental and fire disasters.

All of the process control instrumentation we use in actual product processes are designed to calculate balances but a number of things can happen that can cause surprises:

1) A reaction, with a very slow kinetic rate constant (more later), may be forming a material in the process that was unanticipated. Depending upon the downstream processing and how the anticipated products are handled (distillation, filtration, crystallization, etc.), this material may "bleed" out of the system after building up to a certain level. So eventually the mass balance will close, but in a short or intermediate time frame, it may not.

Chemical Engineering for Non-Chemical Engineers, First Edition. Jack Hipple.

2) An unanticipated liquid reaction product, with a boiling point, which interferes with a distillation separation downstream, can cause a temporary buildup of material.
3) An unanticipated solid reaction product that precipitates out of solution and builds up in process equipment, possibly blocking process piping.

We can consider a very simple example of a material balance for boiling a salt solution to increase its concentration, as shown in Figure 3.1. Let's assume that we have 100# of a 10% salt solution entering an evaporator, and we want to increase its concentration to 50%. How much water has to be evaporated? Let's first start with the feed stream. We have 100 total pounds with 10% salt, so 0.10×100 means there are 10 pounds of salt in the feed stream. That also means there must be 100 – 10 or 90 pounds of water in the feed. How much salt is in the concentrated product coming out of the evaporator? Since we know that salt does not have a vapor pressure and will not boil, we know that *all* of the salt must be coming out of the evaporator, meaning there is also 10# salt leaving the evaporator. How much water (x) was evaporated? We can calculate this with a simple mass balance calculation. If there is 10# of salt leaving the evaporator (the same as entered) and the solution is 20%, then the amount of water leaving the evaporator can be calculated as follows:

$$10 = 0.20\left(y\right),$$

where y is the total solution amount.

$$y = \frac{10}{0.20} = 50 \text{ pounds of total solution}$$

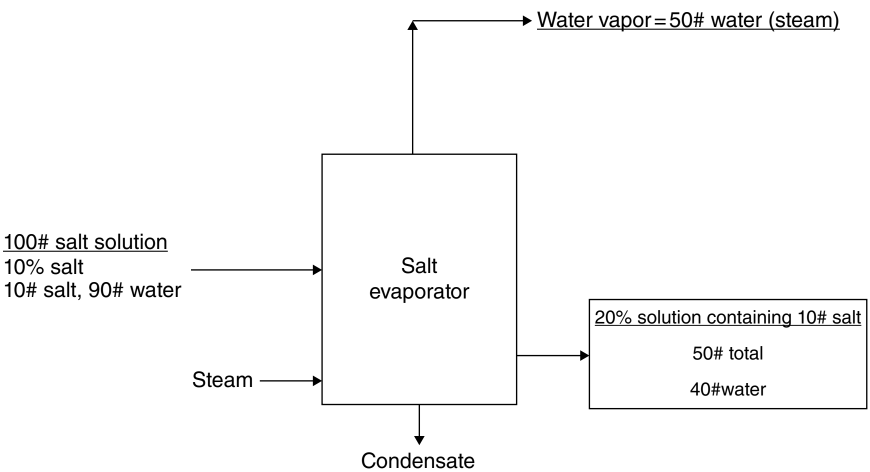

Figure 3.1 Salt evaporator material balance.

Since we know that the solution leaving contains 10# of salt, the remainder must be water, so the water leaving the bottom of the evaporator is 50 – 10 or 40#. How much water is evaporated? The material balance on the water shows us that this must be 90 – 40 or 50# of water. This calculation is shown in Figure 3.1.

If we were measuring one or more of these variables and the balance did not "close," then that indicates a problem that could be any one of these:

1) The steam supply is inadequate to evaporate as much water as desired.
2) The concentration of the incoming salt solution is less than designed.
3) The rate of product leaving the evaporator is not what it is expected to be.
4) The concentration of the salt solution leaving the evaporator is not as desired.

Just the simple concepts of mass balances can generate serious troubleshooting questions to be explored by the people running the evaporator. This may be made easier with any number of online instrumentation systems, but the simple concepts of material balance ("what comes in will come out eventually") can focus the analysis. The accuracy and calibration of instrumentation such as weigh cells, flow meters, and concentration measurements can be critical in determining accurate material balances.

Another important aspect of balances is where we draw the boundaries. Let's take a look at a system where a slurry (a liquid containing suspended solids) is being pumped into a settling tank where solids settle out and the settled solids are drawn off in parallel with the clarified water (see Figure 3.2).

If we draw a box around the entire operation, we would expect that, over time, the amount of slurry entering the tank would equal the amount of water and the amount of enriched or concentrated solids to be equal.

However, we could draw the box at the point shown in Figure 3.3.

In this case, the amount of slurry entering the feed line must equal what actually enters the settling tank. If it did not, there is a leak in the pipe, or some of the solids are accumulating in the pipe, potentially plugging it if left unchecked.

We could also draw the system boundary for a mass balance around the tank itself as shown in Figure 3.4.

In this case, we are measuring the input slurry mass and the mass in the tank. In its initial start-up, we would not expect this mass balance to "close" as the tank will fill up to some predetermined level prior to water overflowing and possibly solids building up to a point where they can be lifted out of the tank.

In Figure 3.5, we see the total system mass balance. If, after some operating time, the sum of the mass of slurry in the tank did not equal the sum of the mass of solids and clarified water leaving the tank, it could indicate:

1) There is a leak in the system in the entering pipe (prior to its entry into the tank), the tank itself, or the clarified water outflow pipe.

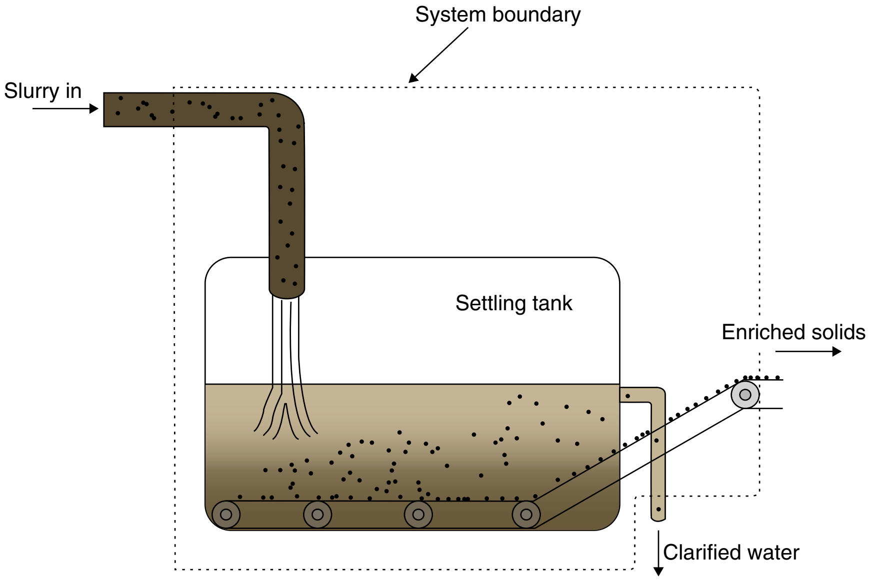

Figure 3.2 Slurry settling and concentration process.

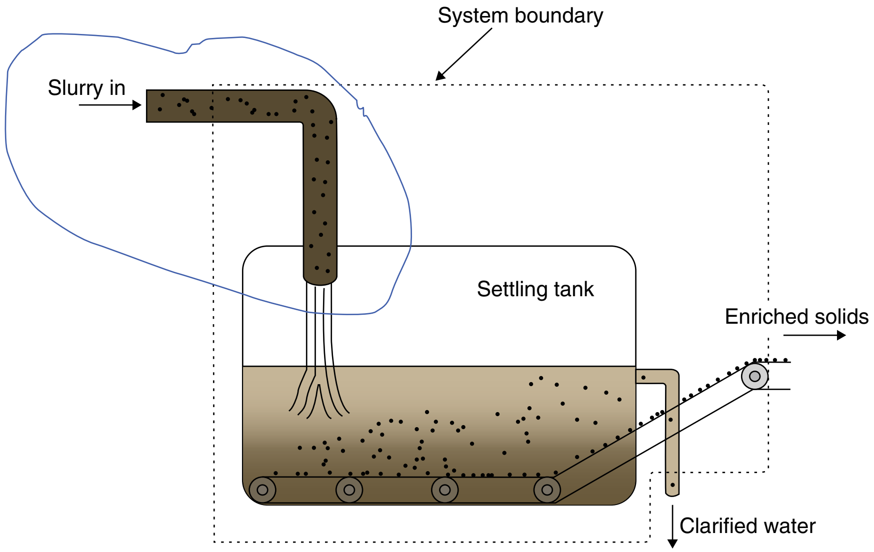

Figure 3.3 Mass balance around feed pipe.

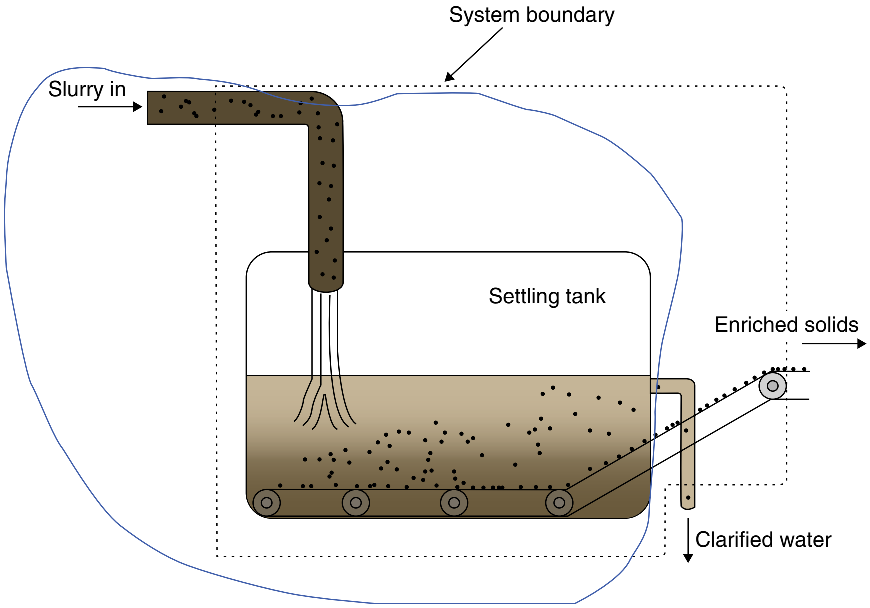

Figure 3.4 Mass balance around the tank alone.

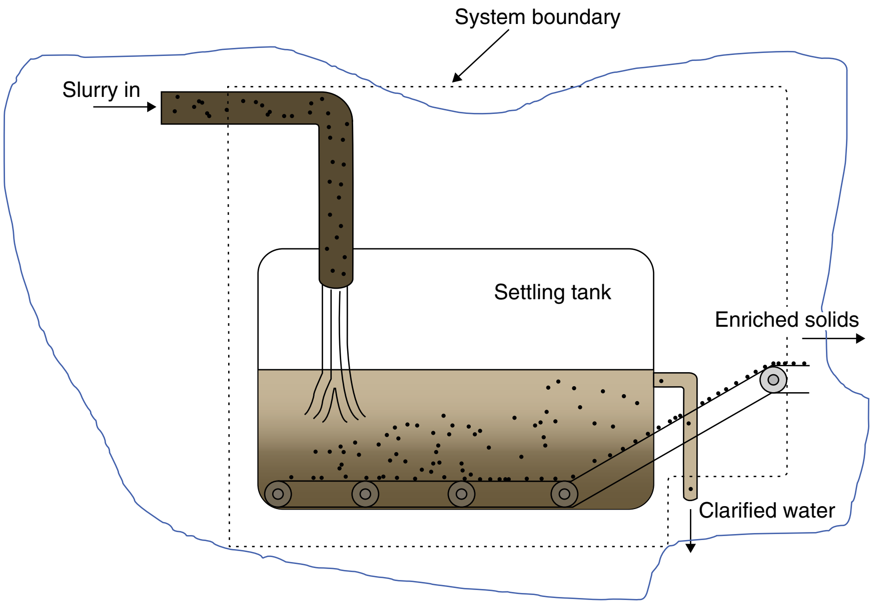

Figure 3.5 Mass balance versus time and boundary—accumulation.

2) The solids are filling the tank and not being removed.
3) An unanticipated chemical reaction generating a gas, which is leaving the system through a vent pipe or building up pressure within the tank.

You might think of other possibilities as well. These kinds of consequences, none of them desirable, are the key reasons that an online material balance in a manufacturing process is critical and usually incorporated into its process control and measurement systems.

Energy Balances

The concepts here are the same, but the factor of heat being generated or absorbed during a chemical reaction must be taken into account. We can express this type of balance as

Energy in = energy out + energy generated + energy stored

Energy generated could be negative if the reaction is endothermic (heat absorbing, more later).

In the previous example of the salt water evaporator, the mechanism of boiling the water away from the solution is to introduce steam, allowing it to "condense" and giving its energy value to the salt solution in sufficient quantities to boil the solution. If the amount of steam we introduced was less than this amount, the solution would not boil, but would merely get warmer. When we are discussing the energy balance aspects of this diagram, there are some more things that must be considered:

1) The energy content of the steam will depend on its pressure.
2) How much heat the solution can absorb will depend on its heat capacity, which in turn, will depend on its salt concentration.
3) The boiling temperature will be affected by the pressure in the evaporator as well as the liquid "head" in the evaporator.
4) Energy can be lost to the surroundings. This will be affected by what type and the amount of insulation and the temperature difference between the vessel and its surroundings.

If we have a chemical reaction occurring during the process, it could be exothermic (heat generating) or heat consuming (endothermic). The values of these reaction energy releases would be taken into account, along with the temperatures, flows, and heat capacities in calculating an online energy balance. If these numbers do not "close" or balance, there are a number of possibilities:

1) Flows are not as expected, not only in an absolute sense but also in a ratio or stoichiometric sense.
2) Temperature measurements are not correct.

3) External energy (heating or cooling) input is not what is planned.
4) If the flows are incorrect, then what may happen to the heat generation or release that is expected?
5) Lack of complete understanding of the physical properties of the materials, such as heat capacity or thermal conductivity.
6) Lack of understanding of the reliability of supporting utility systems such as refrigeration and cooling water.
7) Lack of consideration for physical mixing energy input into a system from internal process equipment such as agitators.

Momentum Balances

The energy represented by fluids and gases in motion (or for that matter, *anything* in motion) must also be conserved and balanced. We use the term momentum to describe this property. For example, if a process valve were to be suddenly shut, when it is normally open with a liquid or gas flowing through it, the energy represented by the flowing liquid will be dissipated in some way. The pipe may vibrate or burst, for example. Consider the case of a simple pipe diameter change, with a fluid (gas or liquid) moving, as seen in Figure 3.6.

Since the mass of fluid flow does not change when the pipe diameter changes, the velocity of the fluid must increase to maintain the same flow rate. In effect, the product of mass × velocity remains the same, and the momentum balance is "closed." The larger the ratio of pipe diameter change, the greater the increase in velocity will be. The opposite would be true if we expanded the pipe diameter—the velocity would slow in proportion to the diameter change.

If we were pumping liquid at a certain flow rate into a system, there is a certain amount of energy associated with this flow. There will be pressure drop in the pipeline and across valves, which when subtracted from the initial input "momentum," should equal the outlet pressure of the stream. If it does not, what might be happening?

1) The flow measurements are not correct.
2) The pressure measurements are not correct.
3) The pipe is leaking!

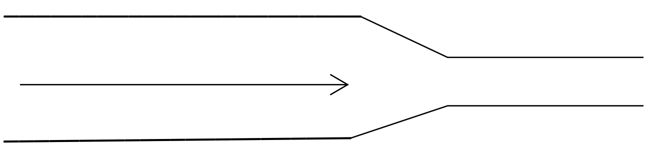

Figure 3.6 Reducing pipe size.

The details of some of these concepts, that is, fluid flow, heat transfer, and evaporators, will be discussed in more detail later, but these basic concepts regarding balances are essential to any chemical engineering analysis, and courses related to these concepts are usually the first courses taken in chemical engineering curricula.

In all cases, the laws of conservation of matter, energy, and momentum must be followed. This is true no matter what aspect or unit operation of chemical engineering we are discussing.

Momentum (fluid energy) and energy balances must also be defined in terms of time and scope as we discussed in detail for mass balance concepts.

Summary

It is essential that complete balances on mass, momentum, and energy for all equipment and processes be known, understood, and continuously calculated and updated. The effects of physical property changes must be considered. They must be tied into appropriate alarm and safety systems. It is also critical that operating personnel receive sufficient education about the processes to be able to observe and respond to situations where balances do not "close."

Coffee Brewing: Balances

How does the concept of balances apply here? Have you ever overfilled a water reservoir in a coffee brewer? Overfilled a coffee cup? What goes in must come out—eventually. Most coffee brewers have hot plates on which a carafe sits. Where does this energy go? For one thing it supplies enough heat to "balance" the heat loss from the carafe to the surrounding environment. The amount of energy is usually more than that, causing the water in the coffee solution to evaporate. If we were able to collect the evaporated water and measure the heat lost by the carafe, we would find it equal to the energy supplied to the hot plate. Have you ever put an extra filter in a machine to make sure that there are no coffee grounds dropping into the cup? You probably remember a few times when the water overflowed before it reached the carafe. The momentum of the water dripping into the filter was constant, and when the filter supplied too much back pressure, the momentum was maintained by the overflowing liquid.

Discussion Questions

1 Are all the mass and energy balances around each of your unit operations measured online and understood? What physical properties would affect these calculations, and are they known or measured? Or just estimated? How "off" do these properties need to be to have a problem? What kind of problem?

2 Are all aspects of fluid and gas energy accounted for? What happens if flow rates increase or decrease? What physical property data changes might affect?

3 Are inventory tanks properly monitored? Are flows in and out measured and balance continuously made? What is the response if the balance does not close?

4 How does your process control and instrumentation calculate mass, energy, and momentum balances? How are discrepancies reported? Handled? Alarmed?

5 When your plant makes changes in your process, how are these concepts of balances used? How could they be used? Are they sufficiently included in other review processes?

6 If there was a major discrepancy in a balance calculation (either manual or via instrumentation), what are possible environmental consequences? How are they monitored?

Review Questions (Answers in Appendix with Explanations)

1 The concept of balances in chemical engineering means that:
A __Mass is conserved
B __Energy is conserved
C __Fluid momentum is conserved
D __All of the above

2 If a mass balance around a tank or vessel does not "close" and *instrumentation readings are accurate*, then a possible cause is:
A __A reactor or tank is leaking
B __A valve or pump setting for material leaving the tank is incorrect

C __A valve or pump setting for material entering the tank is incorrect
D __Any of the above

3 If an energy balance around a reaction vessel shows more energy being formed or released than should be (*and the instrumentation readings are correct*), a possible cause is:
A __Physical properties of the materials have changed
B __A chemical reaction (and its associated heat effects) is occurring that has not been accounted for
C __Insulation has been added on the night shift when no one was looking
D __A buildup of material is occurring

4 If pressure in a pipeline has suddenly dropped, it may be because:
A __A valve has been shut not allowing fluid to leave
B __A valve has been opened, allowing fluid to leave
C __It has calmed down
D __A downstream process has suddenly decided it would like what is in the pipe

5 Ensuring accurate measurements of pressure, flow, and mass flows is critical to insure:
A __We know what to charge the customer for the product made that day
B __We know when to order replacement parts
C __We know how to check bills from suppliers
D __Knowledge of unexpected changes in process conditions

Additional Resources

Hatfield, A. (2008) "Analyzing Equilibrium When Non-condensables Are Present" *Chemical Engineering Progress*, 4, pp. 42–50.
Ku, Y. and Hung, S. (2014) "Manage Raw Material Supply Risks" *Chemical Engineering Progress*, 9, pp. 28–35.
Nolen, S. (2016) "Leveraging Energy Management for Water Conservation" *Chemical Engineering Progress*, 4, pp. 41–47.
Richardson, K. (2016) "Predicting High Temperature Hydrogen Attack" *Chemical Engineering Progress*, 1, p. 25.
Theising, T. (2016) "Preparing for a Successful Energy Assessment" *Chemical Engineering Progress*, 4, pp. 44–49.