

**FUNDAMENTALS OF EVAPORATION AND EVAPORATORS
FOR PLATING BATH AND RINSE WATER RECOVERY
IN THE SURFACE FINISHING INDUSTRY**

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Fundamentals of Evaporation and Evaporators for Plating Bath and Rinse Water Recovery in the Surface Finishing Industry

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This paper presents an overview of important physical and chemical considerations, and energy requirements, governing the design and selection of atmospheric and vacuum evaporators for plating bath and rinse water recovery, and for the volume reduction of pretreated waste water in the Surface Finishing Industry. Single stage atmospheric and vacuum and other evaporator designs are compared.

Introduction

Evaporation is the oldest and most broadly applied of the separations technologies and has an extensive operating history. In the Surface Finishing Industry, evaporative recovery is classified as a concentrate and return technology and its track record and benefits are well demonstrated.

Evaporation is routinely used for point source separation and recovery of plating baths and their associated rinse waters for recycle to the finishing system. Evaporation is also being used successfully to minimize liquid discharges from manufacturing plants by concentrating certain pretreated waste waters, or brines, for haul-away and disposal while recovering additional process water for recycle to the process.

Compared to other separations methods, evaporation is more energy intensive. However, it is the only recovery technology which can treat plating rinse waters to separate the solvent (water) from the dissolved chemicals and concentrate the remaining solution back to, or even beyond, bath strength.

A basic understanding of the physical and chemical laws governing the behavior of solutions of dissolved substances during concentration, and of the energy requirements for evaporation, will help with the selection and application of evaporators for waste minimization and resource management.

General Chemistry Considerations

Every chemical solution is made up of at least one solvent, and one or more dissolved materials referred to as solute. Water is the major solvent used in the metal finishing industry. Most of the chemicals used by the metal finishing industry are water soluble.

Fortunately, most solvents, including water, have high vapor pressures and readily vaporize when exposed to heat. Most of the bath chemicals used for plating are essentially non-volatile and exhibit little or no vapor pressure, even if heated to very high temperatures.

This wide difference in vapor pressure (or relative volatility) between water and bath chemicals is what facilitates separation of bath drag-out from rinse water.

Separation and Recovery by Evaporation

By definition, evaporation separates volatile substances (water) from non-volatile materials (dissolved salts, or plating chemicals) by means of heat energy induced phase change or vaporization of the water, which can be condensed and recovered for reuse. The amount of water removed by vaporization determines the final concentration of the recovered bath.

Evaporation is most effectively used to concentrate dilute chemical solutions to produce a liquid concentrate. While not usually necessary, and depending on the bath chemistry involved, evaporation can in most cases further concentrate recovered solutions up to, or close to, the limit of solubility of the dissolved chemicals -- to the point where solids begin to form. If continued beyond that point, and with the application of additional specialized drying equipment, a solid slurry or dry solid can be produced.

Energy Requirements

Heat energy is required to evaporate water from an aqueous solution. The amount of energy required is roughly 1000 Btu per pound mass of water evaporated, regardless of whether the evaporation is conducted at atmospheric pressure or under vacuum. There is no exception to this rule! Call it the rule of 1000.

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To evaporate a pound of water, this quantity of heat energy must be supplied from some energy source. With the possible exception of an unlimited supply of hot, dry desert air, or of waste process heat which could be captured for use, vaporization energy is rarely free.

Heat energy only flows downhill; that is, from a hot body to a cooler body. If there is no difference in temperature between two bodies, there will be no transfer of heat energy between them.

The greater the temperature difference between a hot and a cooler body, the greater and more efficient will be the heat flux, or rate of heat transfer. At higher rates of heat transfer, heat exchangers will be smaller, more efficient and generally less costly.

Low pressure steam is the most common heating medium used by plating operations. Evaporator designs are available for heating with low pressure steam, with hot water, or for direct or indirect heating by electric power.

Physical & Chemical Considerations

Boiling Point Elevation

Water is volatile and its tendency to evaporate increases with an increase in temperature and a decrease in pressure.

When chemicals are dissolved in water, the equilibrium vapor pressure of that solvent water decreases below the normal vapor pressure of pure water solvent at any given temperature. The more chemical that is dissolved in the water, the more the vapor pressure of the water will be depressed.

A decrease in the vapor pressure above a boiling aqueous solution automatically decreases the rate of evaporation and makes it increasingly more difficult to vaporize and separate water from the solution. (Fig.1)

However, the operating vapor pressure above a boiling liquid, and the boiling temperature of that liquid are established and controlled by the design and operating pressure, or vacuum, in the evaporator. As shown in Figure 1, and at a given operating pressure, the boiling temperature of the solution automatically increases, or elevates, to maintain a constant vapor pressure above the boiling liquid.

This phenomenon will occur regardless of whether the operation is conducted under vacuum or at atmospheric pressure, and is referred to as Boiling Point Elevation (BPE).

BPE is different for each dissolved chemical and is best determined by direct measurement for any given solution. The individual BPE for most plating chemicals ranges from as little as a few degrees to as much as 20-25 Fahrenheit degrees depending on the chemical. This increase in boiling temperature over a concentration cycle has a major impact on evaporator output and operation.

To illustrate; for an evaporator designed to operate with a respectable thermal driving force of, say 50 F° for example (the difference between the steam temperature and the boiling point of the solution being concentrated), a 10 or 15 degree BPE will decrease that 50 degree temperature differential to a 35 degree differential which will reduce the evaporation rate, or output, of the system proportionally.

To compensate for the projected fall-off in evaporation rate as the concentration of the recovered bath increases, additional heat transfer surface area should be factored into the design of the evaporator boiler section by the supplier, particularly if a minimum recovery rate of water distillate is required.

The Impact of Chemical Solubility

Most water soluble chemicals absorb heat when they dissolve. Furthermore, their solubility increases as solution temperature is increased up to the point of saturation, or the limit of solubility of the specific chemical at that temperature. The saturation point, or solubility limit, differs for each chemical.

It also follows that the cooler the solution, the less chemical will dissolve or remain dissolved, and the saturation point decreases with a decrease in solution temperature (an argument against concentrating at too low an operating temperature).

Conversely, there are some substances which evolve heat when dissolved in water. Such substances become less soluble as solution temperature increases. This is referred to as an inverse solubility characteristic. These are the materials which usually precipitate and contribute to scale formation on recovery equipment, particularly on column packing or grids and on evaporator heating surfaces.

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Examples of chemicals that exhibit inverse solubility are calcium sulfate and sodium sulfate.

Also, chemical reactions can occur in plating tanks to form insoluble substances or reaction by-products. Examples of such by-products are barium sulfate and barium chromate, which are produced when barium carbonate is added to a chromic acid bath to adjust the chromic acid / sulfate ratio.

Another notorious family of insoluble materials, which form as a result of the presence of iron in phosphate or pyrophosphate baths, is iron phosphate and iron orthophosphate complexes. If not removed by settling or filtration, these substances will eventually drop out as solid scale in an evaporator, or in any other recovery equipment, and are difficult to remove.

Over time, scale usually forms on the heat transfer surfaces of most evaporators. Water soluble materials such as nickel salts or boric acid, which will salt out if the recovered solution is over-concentrated, can be easily removed by flushing the evaporator with dilute feed or water.

Other scaling materials, such as silica, can be removed by periodic chemical cleaning. The more refractory types of scale are best removed by mechanical or hydrocleaning techniques. In certain cases, scale retardants can be metered into the evaporator if the system chemistry will accommodate them.

When concentrating or dewatering pretreated, mixed effluent streams or brines, the pH of the stream should be adjusted to a neutral or slightly alkaline value to avoid unwanted chemical reactions, the production of low solubility products, or the possible decomposition of certain chemicals or release of acid gasses.

Also, in such mixtures, the solubility of a given salt is affected by the presence of other dissolved salts in the solution, particularly those with common ions such as chloride, sulfate or sodium. This is known as the common ion effect.

The presence of a common ion(s) changes the relative solubility of each salt and will drive a portion of one or more substances out of solution to satisfy what is known as the solubility constant, which is a fixed value for each soluble salt.

When pretreated brines are concentrated, the distribution of constituents between the saturated liquid phase (which is usually returned to the evaporator) and whatever solid phase settles out of

solution upon cooling, may differ substantially from the solubility values for single salts. Trial concentration tests are the most practical way to determine the salting characteristics of a given waste stream.

The foregoing review of energy requirements, and of the key chemical and physical principles governing thermal separation and recovery of plating baths and rinse water, will hopefully help the reader to understand and accept the proposition that it is the plating bath and rinse water chemistry that governs what can be achieved by evaporative concentration, and at what cost.

Atmospheric & Vacuum Evaporation

Today, the two most commonly used evaporator designs employed by the Surface Finishing Industry for bath recovery from rinse water are the single stage atmospheric and the single stage vacuum designs.

Atmospheric evaporation utilizes heat energy and a moving air stream to extract and transfer water from liquid feed to the air stream.

Vacuum evaporators generate water vapor by transferring heat energy to the feed stream using surface contact heat exchangers to boil the liquid under controlled conditions at reduced pressure and temperature.

Atmospheric Evaporators

Atmospheric evaporators are essentially simple scrubbing devices which use an air stream to strip water as vapor from a liquid solution. In essence, an atmospheric evaporator is an air stream humidifier. They have been widely used by industry because of their low cost and operating simplicity. Atmospheric units are generally applied singly or in multiples to dewater various plating rinse waters to recover bath concentrate. (Fig. 2)

Atmospheric evaporators operate by either pushing or pulling an air stream through a mesh bed or gridwork over which rinse water, or in some cases, the bath itself, is circulated. Either the air stream or the bath, or both, must be heated to provide the necessary 1000 Btu of heat energy needed to evaporate each pound of water. As indicated at the

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beginning of this article, there is no exception to this energy requirement for single stage evaporators. Heat must be supplied from somewhere or the unit won't function.

The amount of water removed with each pass is a function of the mass, temperature and humidity of the air stream, and of the temperature of the liquid being circulated through the unit. Heat energy is usually supplied by an external heat exchanger. If a normally hot plating bath is being circulated through the evaporator, the total heat energy required may be provided entirely by the bath itself which, of course, will have to be reheated

In most atmospheric evaporator designs, the vaporized rinse water is not captured. Instead, the humid air stream is vented to atmosphere. To avoid possible carry-out and discharge of hazardous substances, the air stream may require additional scrubbing through a neutralizing or water irrigated vent scrubber before final discharge

One recent atmospheric evaporator design has added a condenser and closed the air circuit to eliminate or minimize potential exhaust emissions. A much larger condenser is required to condense water vapor from a stream of air than would be required if air was not present. The presence of an inert gas such as air in the exhaust vapor stream reduces normal condensing coefficients by 90% or more.

An interesting application which is well suited to atmospheric evaporation involves the recovery and simultaneous cooling of hard chrome baths, which often require external cooling to remove excess heat created during plating by high operating amperage.

In such circumstances, both rinse water and bath may be blended for de-watering by the evaporator. In cases where the quantity of heat generated by the electric power demand of the bath is not adequate for the evaporation duty, the addition of external trim heat may be required.

In this special application, operating energy is usually considered to be "free" although it has in fact been paid for as electric power which is very inefficiently utilized by the hard chrome plating chemistry, and which would otherwise be lost as waste heat.

Potential sources of "free" energy which could be used to operate either atmospheric or vacuum evaporators include manufacturing processes with

substantial stack heat losses or facilities located in a hot climate where a supply of hot, dry, low humidity air is available.

Atmospheric evaporators are not considered to be energy efficient.⁽²⁾ At the minimum, a pump is required to circulate the solution to be concentrated.

There are inherent inefficiencies in moving and heating large volumes of air. Spray temperatures must be high. Solution boiling points are higher at atmospheric pressure than under vacuum operation which results in a lower effective temperature differential or thermal driving force .

Despite the simplicity of design and lower initial capital cost, these factors conspire toward higher energy consumption, by an estimated factor of at least 10% beyond the theoretical requirement per pound of water evaporated when compared to single stage vacuum evaporation.

Please note: while this is a reasoned conclusion based on discussions with users and suppliers, the reader should be aware that no specific studies have been published to the writer's knowledge to support this estimate.

Also, atmospheric units are not usually heavily instrumented. Instrumentation consists mainly of temperature, level and electric controls. The vagaries of changes in feed concentration and composition, of air stream and liquid feed temperatures and of the relative humidity of the air stream, contribute to variable process control, variable output and varying product concentration.⁽¹⁾

Atmospheric evaporators and the plating systems they service should be carefully monitored and operated to prevent or minimize foaming in the evaporator caused primarily by the overuse of surfactants or wetters in the plating baths, to minimize potential oxidation of susceptible bath constituents from exposure to air and to prevent overconcentration and possible salting-out and plugging of evaporator internals.

Various suppliers offer a number of basic atmospheric units which are fabricated of molded FRP, PVC or polyethylene and are preassembled, wired and piped. In today's market, it is fair to say that, despite the foregoing technical characteristics and limitations, attractive price and simple operation have made small atmospheric evaporators ubiquitous in the industry, which considers them to

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be adequate for numerous, small bath, static rinse and running rinse dewatering applications.

Vacuum Evaporators

Vacuum evaporators have been used successfully for more than thirty years by the Surface Finishing Industry for point source recovery of plating baths and rinse waters. They are somewhat more complex and require a higher initial capital investment than single stage, non condensing atmospheric units.

Vacuum evaporators are instrumented for push button, fail safe operation and provide close and consistent control of the recovered bath concentration.

There are two main categories of vacuum evaporator; single effect (single stage) and multiple effect. All vacuum designs are devices for distilling a liquid phase at reduced temperatures in the absence of air and producing water distillate as a by-product.

Vacuum evaporators, as employed by the plating industry for bath and rinse water recovery, are usually single stage units consisting of a heated boiler section, a vapor/liquid separator section, a water vapor condenser, a vacuum circuit and a control circuit. The boiler and condenser sections may be arranged horizontally or vertically. (Fig. 3)

The most common heating source is low pressure steam. Units are available to accommodate hot water and electrically driven heat pumps.

The question is frequently asked, "why is vacuum used?"

Operating under vacuum

- 1) reduces the boiling temperature of the bath being concentrated which lessens or eliminates the potential for thermal damage to heat sensitive constituents or additives.
- 2) increases the temperature differential (the thermal driving force) between the heat source and the liquid being concentrated resulting in smaller, more efficient and less costly boiler and condenser designs.
- 3) extracts resident air from the system upon startup and eliminates any possibility of carry-over of hazardous chemicals to a vent stream.

- 4) excludes air from the system which eliminates the potential for air oxidation of recovered chemicals.
- 5) recovers high quality water distillate for return to the plating line.
- 6) desensitizes the system to fluctuations in feed concentration when operated in a concentrate recycle mode.
- 7) eliminates the potential for hazardous air emissions.
- 8) lessens the tendency for scale to form on heating or other surfaces by operating at reduced temperatures.
- 9) provides better management of foam
- 10) reduces the number of pumps required to one, the vacuum pump or eductor circulating pump, whichever is used.
- 11) provides tight process control by recovering bath at an adjustable and repeatable concentration.

The operating vacuum selected, or recommended by the evaporator supplier, is a function of the chemistry of the particular bath being recovered. Baths containing heat sensitive constituents, such as expensive brighteners or additives, are usually concentrated under higher vacuum and lower boiling temperatures than are baths which do not require such constituents.

High vacuum operation requires physically larger evaporators to accommodate the higher specific vapor volumes encountered under those conditions, and to maintain vapor velocities and system pressure drop within design ranges.

The level of vacuum, and thus the boiling point, can be varied within a specific range of vacuum for any given evaporator capacity. But, if an evaporator designed for optimum performance at 11 inches of mercury vacuum is operated below its design vacuum, say, at 26 inches of mercury vacuum, vapor velocities will increase substantially and both the output capacity and product quality will deteriorate.

To satisfy the range of vacuum required by the widely differing bath chemistries used in the Surface Finishing Industry, suppliers of vacuum units have developed a series of standard, off-the-shelf, corrosion resistant evaporator designs to accommodate most bath chemistries and operating requirements.

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The energy demand of a single stage vacuum evaporator is roughly 1000 Btu per pound of water evaporated, or 8400 Btu per gallon of water evaporated, the same as the theoretical energy requirement for atmospheric operation.

Multiple effect evaporators and other specialized designs, such as vapor compression units, are used in the chemical, food and pharmaceutical industries. In most cases, these units are custom designed for specific process requirements.

Multiple effect units are essentially two or more single stage vacuum evaporators in series. Each succeeding stage operates at a higher vacuum or lower boiling temperature than the preceding stage. The difference in vacuum allows the vapor generated in the first stage to heat the second stage which means energy consumption for a double effect unit becomes 50% of that for a single stage unit. (Fig. 4)

If a third stage is added, operating at yet a higher vacuum or lower temperature than the second stage, the overall energy consumption drops to one third that for a single stage system. For each subsequent stage added beyond a second stage, the capital investment and system complexity increase proportionally while the energy savings increases only marginally. Multiple effect units become economically justifiable where large volumes of water or solvent need to be evaporated.

Vapor compression units are generally single stage, electrically driven vacuum evaporators which use a mechanical compressor in place of the vapor condenser to pressurize and increase the heat content and temperature of the vacuum water vapor from the boiler section. The vapor is then used as the heating medium in the boiler where it is condensed as water distillate and extracted from the unit. (Fig. 5)

The relative energy consumption of such a mechanical vapor compression design generally ranges from a very attractive one eighth to one tenth that of a single stage unit (or 100 to 125 Btu per pound of water evaporated). Vapor compression units generally operate at very low thermal differentials, in the order of 2-5 Fahrenheit degrees, and can be rather large in size.

To keep the overall size and price down, the thermal differential would have to be at least 20 Fahrenheit degrees or higher. With only a 20 degree delta T, the unit would still require a large

amount of heat transfer area and the achievable concentration ratio would be low.

High initial cost, an uncomfortably high noise level and restricted corrosion service for commercially available compressors limit the viable applications for this technology in the Surface Finishing Industry.

Evaporation has proved itself over many years and in many applications to be a dependable recovery method. Evaporator/concentrators can generally be operated with minimum attention. If sub-standard performance occurs, the reason can usually be traced to inadequate or improper maintenance or one or more of the following deficiencies:

- 1) Diminished evaporator capacity:
 - a) evaporator starved for steam - either inadequate steam supply or improperly designed steam supply piping resulting in high quantities of steam condensate rather than steam being fed to the evaporator. This occurs more frequently than the reader might suspect.
 - b) scale accumulated on boiler tubes.
 - c) improper setting of concentration sensor resulting in overconcentration and possible solids precipitation in the evaporator.
- 2) Low or diminished quantity of water distillate:
 - a) overconcentration and low evaporation rate.
 - b) inadequate condenser cooling water; impaired supply or scaled condenser due to inadequate cooling circuit or cooling tower maintenance.
- 3) Contaminated water distillate:
 - a) operating at too high a vacuum resulting in high vapor velocity and carryover to the condenser.
 - b) restarting too soon after manual shut down causing burping or flash-over of hot concentrate to the condenser. Concentrate should cool at least 10 F^o, or the unit should be completely drained and refilled before restart.
 - c) operating at too high a steam pressure can cause concentrate blow-by to the condenser.

Lastly, sizing an evaporator to recover a specific plating bath depends on a number of factors such as the hourly bath drag-out rate, bath concentration

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and composition and most important, the rinse ratio, or volume of rinse water required for quality rinsing for every gallon of bath dragged out.

Rinse ratio is directly affected by the number of rinse stations in the rinse system and by their hydraulic arrangement. Every effort should be made to apply counter-current rinse principles to minimize the volume of rinse water needed and thus minimize the evaporator capacity required to process and recover this quantity of water.

Summary

The principal advantages and disadvantages of evaporation and of evaporators can be summarized as follows;

Advantages:

1. Evaporation is a proven, well documented plating bath recovery technology .
2. Provides recovery rates of 90 - 99.9% plus.
3. Reduce waste treatment costs by substantially reducing the quantity of sludge generated.
4. Vacuum operation minimizes losses of heat sensitive bath components from thermal degradation.
5. Wide choice of off-the shelf, single stage designs for both atmospheric and vacuum operation are available to cover most applications.
6. Compatible with most bath chemistries except electroless baths and pickeling, phosphating or chromating rinses.
7. Can concentrate to bath concentration, and can recover both chrome-sulfuric and high chrome etch baths.
8. Evaporators recover the entire bath, not just components of the bath.
9. The concentration of recovered baths is readily controlled by vacuum evaporation.

Disadvantages:

1. Evaporation requires more operating energy than other separation methods.
2. Single stage evaporators have higher overall operating costs than other types of separations systems.
3. While single stage atmospheric units boast low to moderate capital cost, the concentration of the recovered bath can vary.
4. More sophisticated energy efficient vacuum units, such as multiple effect or vapor compression designs, are generally custom

designed for each application and have significantly higher initial cost.

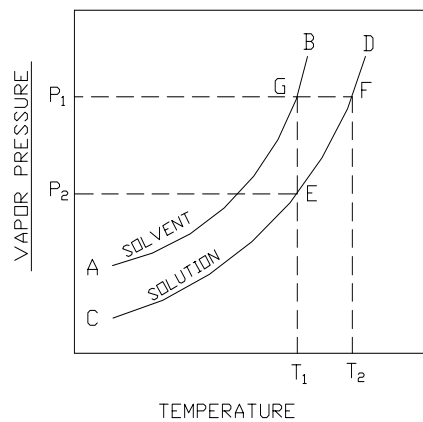
5. To minimize capital investment for any evaporative recovery system, it is strongly recommended to reduce the amount of rinse or bath water requiring evaporation by applying water saving techniques.
6. Separate units are required for each bath.

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BOILING POINT ELEVATION DUE TO DISSOLVED CHEMICALS



$$P_1 - P_2 = \text{VAPOR PRESSURE DECREASE}$$
$$T_2 - T_1 = \text{BOILING POINT ELEVATION EQUIVALENT TO } P_1$$

Figure 1

SINGLE STAGE
ATMOSPHERIC EVAPORATOR

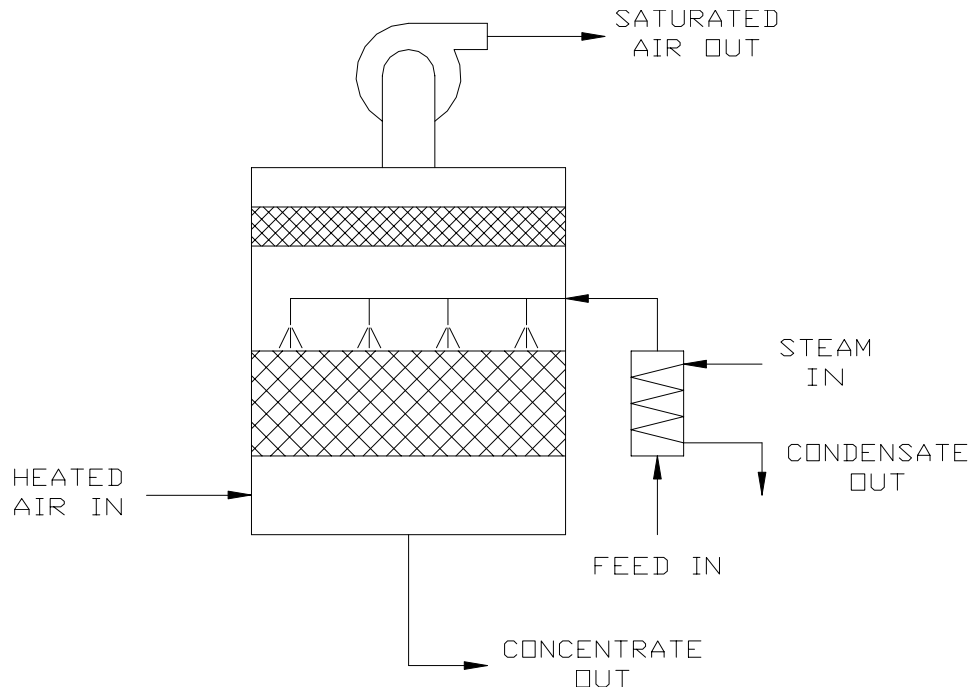


Figure 2

SINGLE STAGE
VACUUM EVAPORATOR

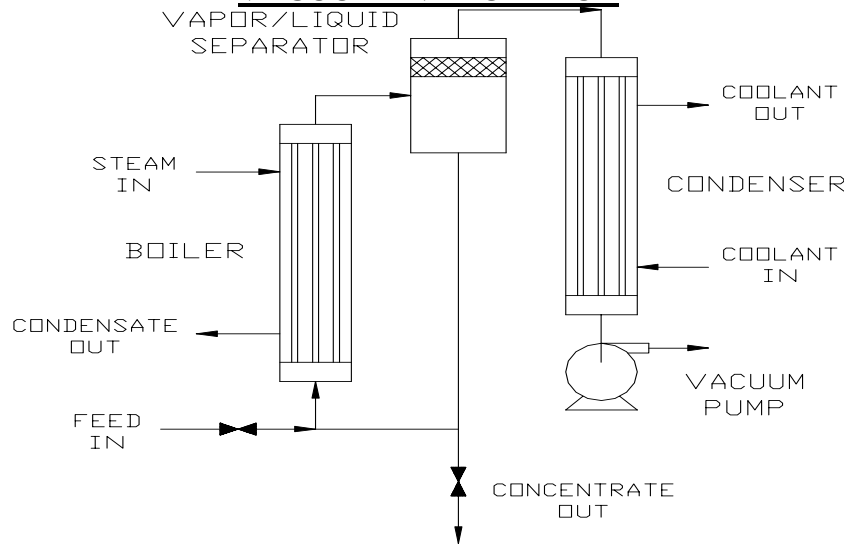


Figure 3

DOUBLE EFFECT
VACUUM EVAPORATOR

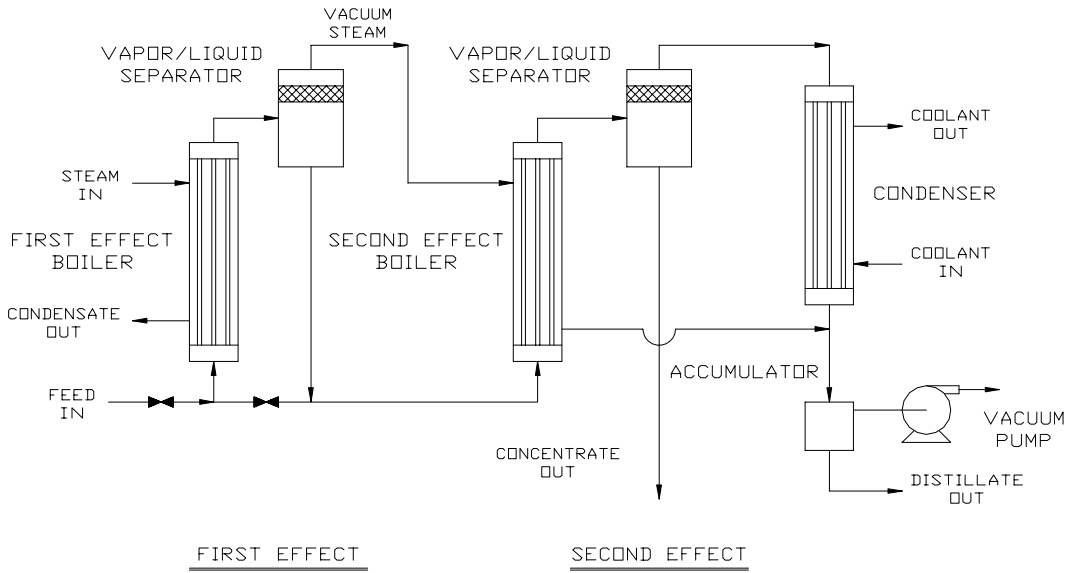


Figure 4

VAPOR COMPRESSION
VACUUM EVAPORATOR

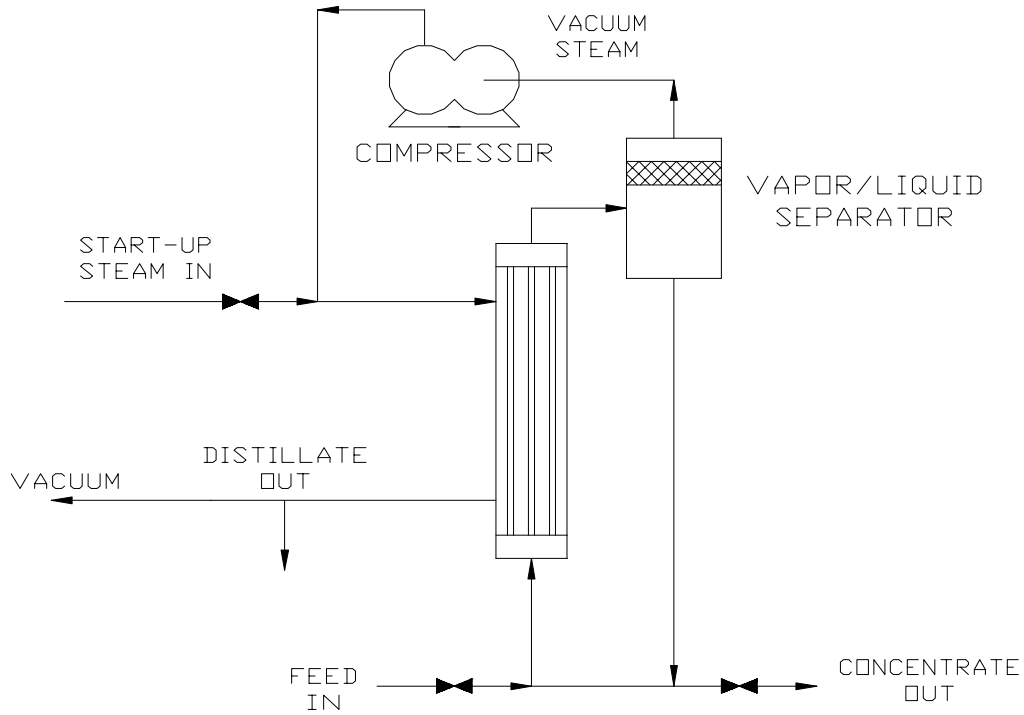


Figure 5