SAFI Application Sheet

Application / Segment :	**Chlor-Alkali plants**
Location :	All
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Introduction

Chlor-alkali plants use salt and electricity to make chlorine, caustic soda, and hydrogen which are used primarily for the production of sodium hypochlorite, ferric chloride, calcium hypochlorite, hydrochloric acid, and other chlorine derivatives.
In such aggressive chemical processes, pressure and temperature are suitable for plastic and SAFI thermoplastic valves are very suitable to this industry.

Applications

The chlor-alkali process was industrialized in 1892, it uses brine (aqueous solution of NaCl - salt) and a large quantity of energy to produce chlorine gas (CL2), hydrogen gas (H2) and sodium hydroxide (NaOH), or caustic soda.

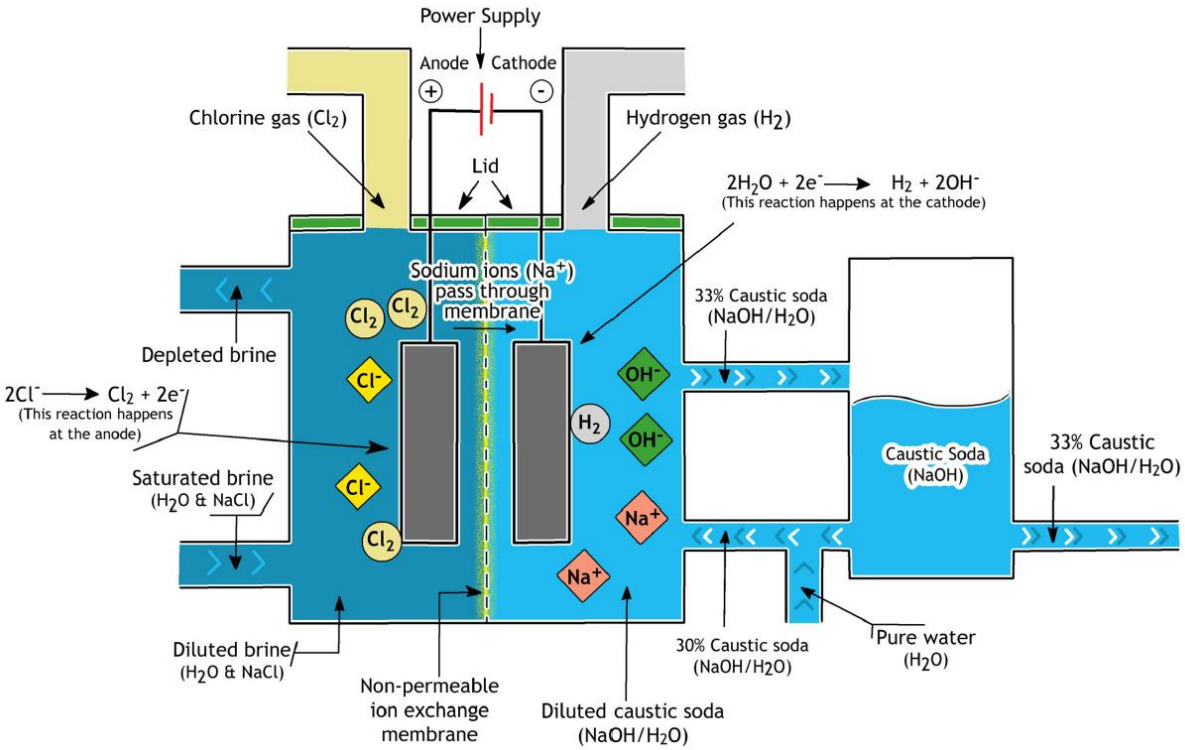
Chlor-alkali process uses three electrolysis technologies: membrane, mercury and diaphragm.

- Membrane cell electrolysis employs permeable membrane as an ion exchanger. Saturated sodium (or potassium) chloride solution is passed through the anode compartment, leaving at a lower concentration. This method is more efficient than the diaphragm cell and produces very pure sodium (or potassium) hydroxide at about 32% concentration, but requires very pure brine.
- Diaphragm cell electrolysis, separates a cathode and an anode, preventing the chlorine forming at the anode from re-mixing with the sodium hydroxide and the hydrogen formed at the cathode. The salt solution (brine) is continuously fed to the anode compartment and flows through the diaphragm to the cathode compartment, where the caustic alkali is produced and the brine is partially depleted. Diaphragm methods produce dilute and slightly impure

alkali, but they are not burdened with the problem of mercury disposal and they are more energy efficient.

- Mercury technology are being closed down due to their environmental impact.

Below: the membrane cell process



Applications for SAFI valves take place on those steps of the chlor-alkali process:

1. Saturated brine
2. Demineralisation unit
3. Purification of salts
4. Return brine
5. Treatment to remove the chlorine in the return brine
6. Wet chlorine gaz
7. Caustic soda loop
8. Hydrogene gaz loop
9. HCL synthesis
10. Sodium hypochlorite production and storage
11. Dry Chlorine gaz section
12. H2SO4 98% pure (storage)
13. H2SO4 98%+ trace CL2 from liquid ring compressors
14. H2SO4 70% to 96% + CL2 from dryers
15. Water treatment unit

1. **Brine**

The brine is a mix of saturated salt + demineralised water that is fed into the electrolyser at room temp. Large butterfly valves in PPH/EPDM can be used for the brine.
For small diameters (up to DN 150), ball valves full PVDF can be used. PVDF has an excellent resistance to abrasion, 100 better than PTFE according to the taber test.

2. **Demineralisation water unit**

The same fluids and process apply here as in any demineralisation water unit, with requirements for plastic valves (see application sheet on demineralization water unit).

3. **Purification of salts**

Impurities in the salt damage the electrolyser and increase power cost. To precipitate the impurities, caustic soda and sodium carbonate are added in the process. For these fluids many sorts of valves (metal and plastic) are normally used. But most of the time the user does not care much at that stage about possible damage.

Filtration systems are also used to collect the impurities and they need to be cleaned from time to time. Valves can be used here also. Each plant has its own way and use different valves, including plastic and plastic pneumatic operated valves.

The last step of purification is a system of iron exchange resin beds (hydrochloric acid and caustic soda). It is the same process as in a demineralisation water unit where lots of valves are needed to recycle the fluid. Valves used: pneumatic automated valves such as Gemu diaphragm pneumatic valves or SAFI ball valves in GRPP.

ELECTROLYSER ROOM

Pressure is 0 bar in the electrolyser and temperature is 90°C. Everything that comes out of the electrolyser is at this same pressure and temperature.

On the Anode side:

4. **Return brine** (weak brine or depleted brine or chlorinated brine) **90°C**

Depleted brine comes back from the electrolizer which contains different chlorine compounds which are difficult to handle. SAFI “classic FKM” valves must be upgraded to class 1 type because the service condition makes classic FKM swell. So the class one SAFI PVDF valve is needed.

What is a **Class 1 SAFI PVDF ball valve**:

- PVDF SAFI flange ball valve
- FEP seals behind the seats, but the groove behind the seat must be machined because the seals get too compressed when they swell and then can break.
- FKM seals everywhere else (no need of Kalrez) but with Eurochlor-approved chlorine-compatible Voltalef® grease on all the seals.

Class 1 PVDF ball valve with pneumatic actuator

5. **Treatment to remove the chlorine in the return brine**

It includes compressed air lines and sulphite (tank + mixer). After removing the chlorine, you can use regular SAFI valves again. Salt is added and returned into the system.

6. **Wet chlorine gas**

Wet chlorine gas that comes out directly of the electrolyser contains 60% water vapour and is rather dirty. The wet chlorine is at 90°C, with concentration of CL2 from 30% to 70%. SAFI PVDF ball valve Class 1 valve can be used here (see above).

Condensate removal:
A large CPVC/GRP, titanium pipe takes the wet chlorine gas out of the cell house. In the pipe, the water vapour condensates and is removed with smaller pipes and valves connected at the bottom of the large pipe. Class 1 valves must be used there.
Isolation class 1 valves for the instruments including analysers can be used here too.

There is no solution in thermoplastic for the rest of the chlorine gas given the harsh service conditions.

Also, when the electrolyser (cell room) starts, it contains air and it is called weak chlorine. This weak chlorine is send to the reactor as it cannot be used for production. When the electrolyser is ready, it delivers pure chlorine and it is call “strong chlorine”.

<u>On the cathodic side:</u>

7. **Caustic soda (NaOH) loop**

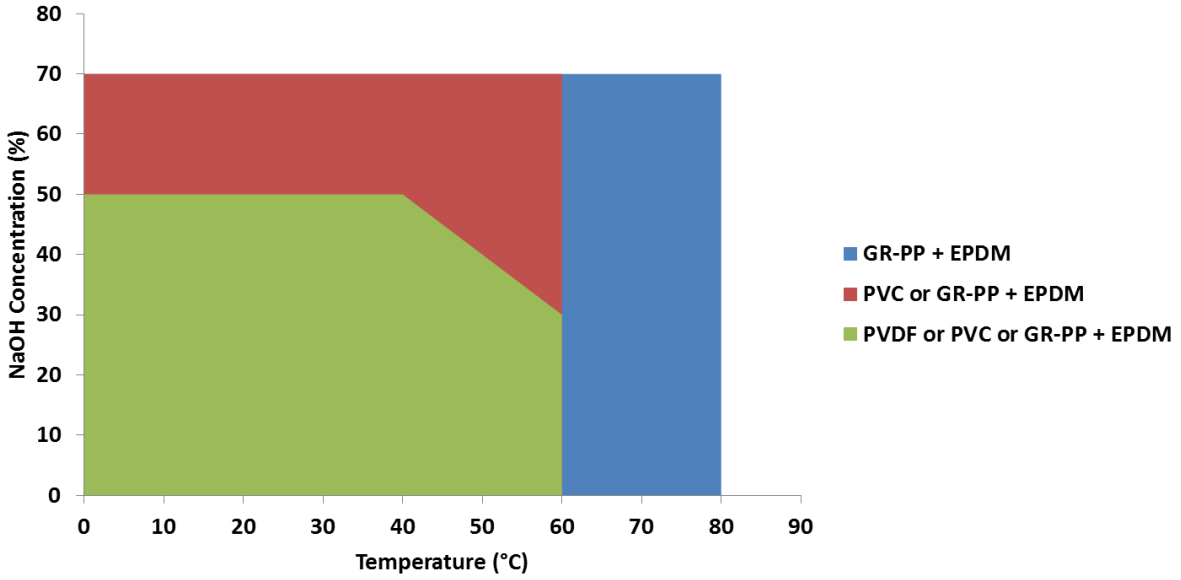
“Weak caustic soda” (15%) is fed into the electrolyser and “strong caustic soda” comes out of the electrolyser (33%) at 90°C. Ball valves in GRPP/EPDM can be used there without problem. Size is maximum 6”.

Some of the strong caustic is then diluted to 15% and returned to the electrolyser.

The **strong caustic soda** is stored in trucks and tanks, where many valves are used, especially in the truck filling station where ball valves (GRPP) and any other kinds are used. In old plants many diaphragm valves are used there for on/off applications only and can be replaced by ball valves.

Some plants will produce up to 50% caustic by evaporating water from the 33%, but this is a hot process and no plastic can be used here.

Some plants dry the caustic soda to make caustic soda flakes or beats. This is also an extremely hot process where only pure nickel resists here.



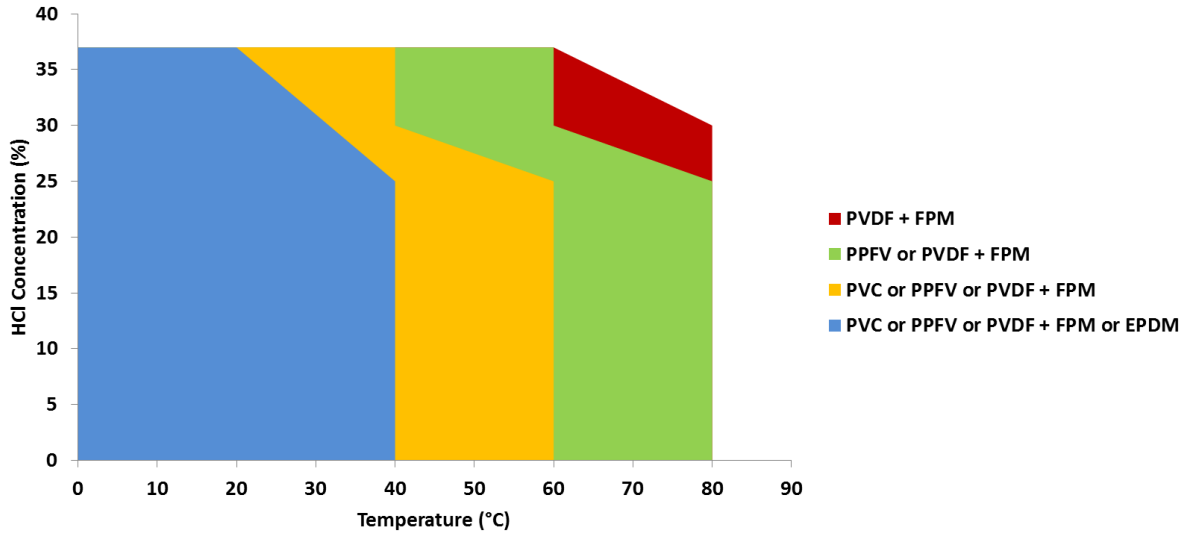
8. Hydrogen gas loop

Mostly any valve can handle the hydrogen, but only very few chlore-alkali plants accept to use plastic valves here (Vinythai, ex-Solvay, in Thailand uses PVDF valves here).

OUT OF THE ELECTROLYSER ROOM

9. HCL synthesis

Hydrogen and chlorine gas are used to make HCL in a reactor. 35% HCL comes out of the reactor at 2 bars, not at a high temperature and is then stored. Here Ball valves in GRPP/EPDM/FKM valves can be used. For truck delivery, GRPP/EPDM/FKM automated ball valves are used here.

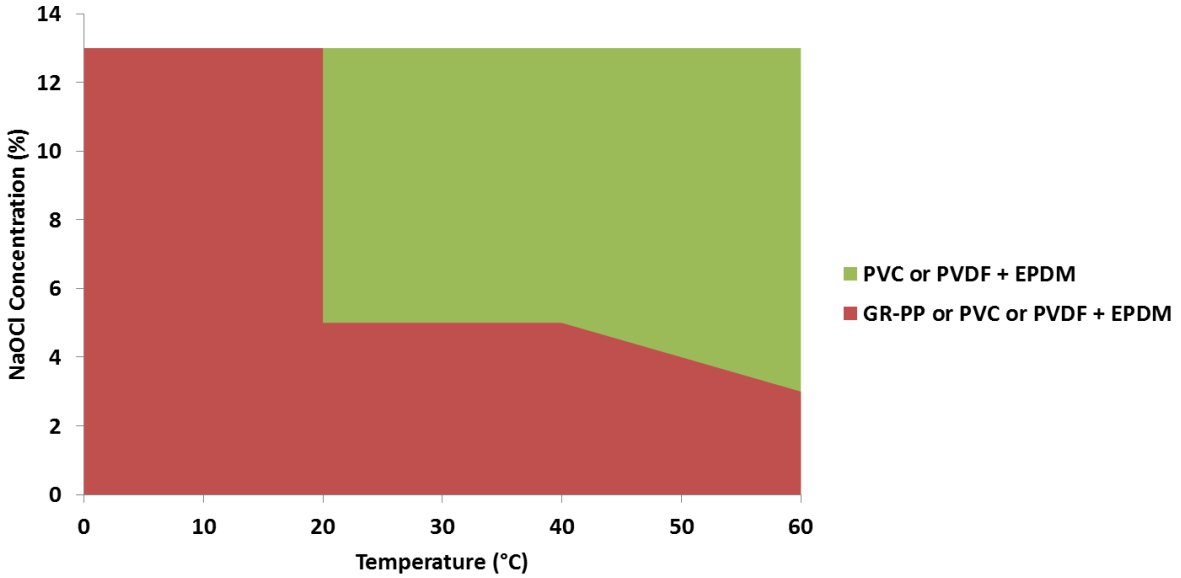


HCL also returns to the plant for the iron exchange bed regeneration and brine acidification. GRPP/EPDM/FKM ball valves can be used for this.

10. Sodium hypochlorite (NaOCL) production and storage

All chlorine plant must have a reserve of sodium hypochlorite as it is used as a scrubber for any release of chlorine. NaOCL is used to capture chlorine emissions from anywhere in the plant (you cannot release chlorine in the atmosphere as it can kill people). Normally, there is a suction network in each plant which sucks the air containing chlorine and sends it to the hypochlorite reactor. The reactor mixes diluted chlorine with caustic soda. You start with fresh caustic soda and circulate it into the reactor until it becomes sodium hypochlorite. Experience and tests must be done before using plastic valves for the hypo reactor (its hot and it's a mix of several chemicals).

The sodium hypochlorite (12% to 13%) goes to storage tank where GRPP/EPDM ball valves are used. Then a delivery section of the NaOCL is there equipped with GRPP/EPDM automated ball valves.
Some plants also feed clean CL2 to the reactor to produce Sodium hypochlorite and sell it.



11. Chlorine gas section (cooling and drying)

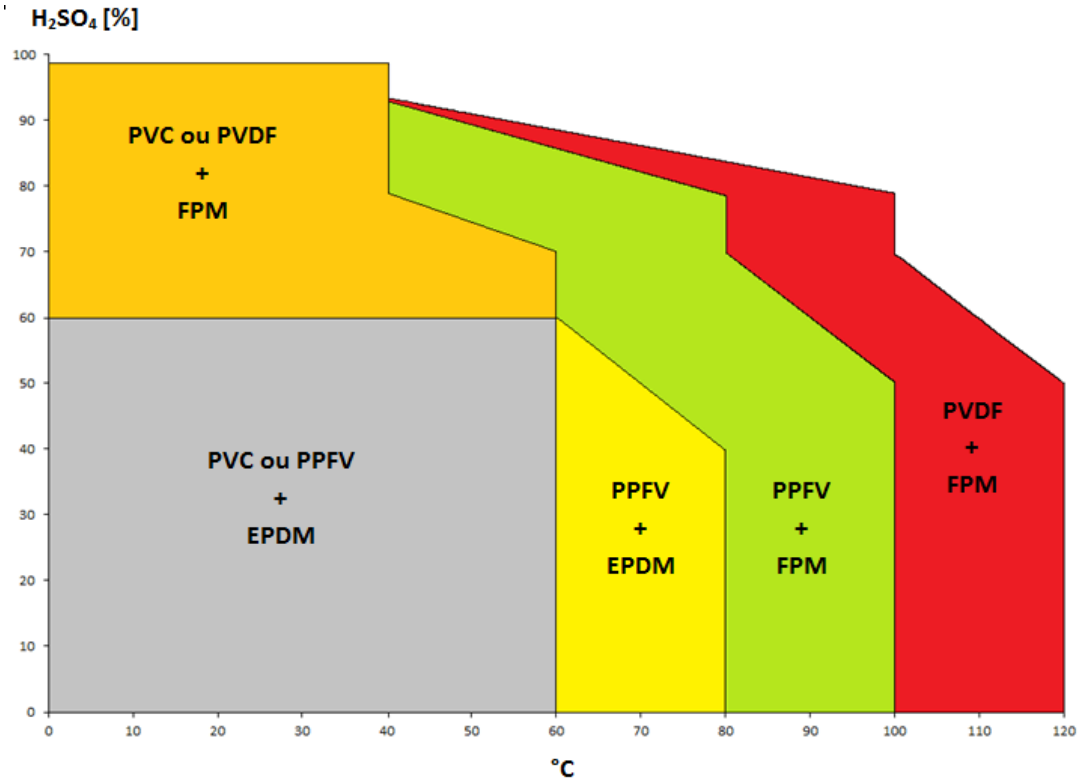
Avoid putting valve on the main line of chlorine gaz.

Chlorine cooling
When CL2 comes out of the electrolyser room (cell house), it condensate in the large pipes (see above), it then becomes dry and is then cooled down in a cooling tower.
Two systems are used for cooling:

- Titanium heat exchanger (no plastic valves)
- CL2 Quench with cold water (direct contact): plastic valves can be used on the water circuit. But water can be mixed with chlorine, so it is better to test the valve before.

Chlorine drying
After cooling, chlorine goes to a drying tower. Sulfuric acid is sprayed in three steps, with different H2SO4 concentrations (60% to 97%), in a tower to dry the chlorine.

The acid loops use pumps and valves where thermoplastic valve in PVDF/FKM work very well. With medium concentration, metal valves suffer from corrosion.



Sulfuric acid is then regenerated in a regeneration plant (this process is sometimes externalised).

After this step, chlorine is dry (in gas shape) and according to Euro Chlore plastic valve must not be used there.

Water treatment unit

Water in needed in several steps of the process, as can be seen above, and chlore alkali plants often have their own water treatment unit on site, where plastic valves are often used (refer to application sheet on water treatment units).

Many other downstream applications

From those ram materials (chlorine, caustic soda, hydrogen, sodium hypochlorite, hydrochloric acid, and other chlorine derivatives) derive many other industries which produce feed stocks for a variety of other chemicals.

Chlorine finds application in EDC/PVC, epoxies, polyurethanes, phosphorus compounds and caustic is used in a large number of processes in the chemical, pulp and paper, textile, food and mineral industries. Chlorine is used to produce hydrochloric acid (HCl), a strong inorganic acid. HCl is used for a variety of applications, from acidification to metal treatment, e.g. as pH adjustment and neutralization. Chlorine is also used to produce Iron Chloride which finds its way in applications such as waste water treatment, drinking water production, cosmetics and even in pharmaceutical products such as medicines.

Caustic soda finds application in the aluminum industry, pulp & paper and the chemical industry. The main applications are water treatment and water purification,

as cleaning agent, or a wide range of uses in chemical industry like starch production or for the desulphurization in the petrochemical industry.

These industries must be approached as well, as they also can use SAFI thermoplastic valves.

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SAFI products used in chlor-alkali plant:

- Ball valve GRPP and PVDF + class 1 + V-port
- Flowmeters
- Sample valves
- Non return valves in front of pumps
- Pressure gages with diaphragm

SAFI valves are appreciated because of the high quality of the materials and reliability of the valve. The design of the valve (with flanges that are fully part of the valve) is also very appreciated. SAFI ball valves in particular are perfectly suitable for most chlore alkali applications and are often replacing diaphragm valves or lined metal valves of “old factories”.

In NCI (National Chlorine Industry in Jordan), SAFI valves replaced PTFE lined metal valves on a chloroparaffins vapor line:

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Clients references (non exhaustive list):

France:

- Solvay 39 Tavaux
- Chloralp 38 Le Pont de Claix
- Atochem 38 Jarrie
- Atochem 69 St Fons

Belgium:

- Tessenderlo
- Umicore
- Ineos
- Solvay

Indonesia:

- Satomo indovinyl monomer, Bojonegara, Kab. Serang ,Java. Manufacturer of EDC and VCM.
- Riau andalan pulp & paper, Pekanbaru, Riau. Pulp mill, Chlor-alkali unit, Chemical plant.
- Indah kiat pulp & paper, Perawang, Riau. Pulp mill, Chlor-alkali unit, Chemical Plant.
- Lontar papyrus, Tebbing Tinggi, Jambi Pulp mill. Chlor-alkali unit, Chemical plant

Malaysia:

- CCM chemicals, Pasir Gudang, Johor.

Singapore:

- Chemical industries far east limited, Jurong Island.

Thailand:

- Vinythai, Map Ta Put, Rayong
- EDC and VCM manufacturer.

Others:

- NCI (Jordan)

For more information on chlore alkali plants: http://chloralkalitechnology.blogspot.fr/