Chemical Injection Primer

Rose Corrosion Services Limited
Regus House, Windmill Hill Business Park
Whitehill Way, Swindon
SN5 6QR – UK
Tel: +44 (0)1635 552225
Fax: +44 (0)1635 568690
Email: sales@rcslgroup.com
Website: www.rcslgroup.com

Rose Corrosion Services Ltd is a subsidiary of:
BAC Corrosion Control Ltd
Stafford Park 11, Telford, Shropshire
TF3 3AY - UK
Tel: +44 (0)1952 290321
Fax: +44 (0)1952 290325
Email: sales@bacgroup.com
Website: www.bacgroup.com

Chemical Inhibitors for Corrosion Control

An inhibitor is a substance that reduces corrosion damage when relatively small amounts of it are present in the corrodent. Inhibitors are classed in many ways; by their composition (organic or inorganic); by the mechanism of their action (anodic or cathodic control); or by their form (solution or vapour). The four generally applied categories are anodic, cathodic, adsorption and vapour phase.

Anodic inhibitors retard the anodic reaction. They are usually either a) oxidising agents (chromates, nitrates, ferric salts) that promote passivity, or, b) film formers that precipitate insoluble films on the anode area (for example alkalis, phosphates, silicates, benzoates). Anodic inhibitors are often thought to be dangerous, particularly the oxidising type, because they must completely protect the anodic areas to be effective. If a small anode area is not protected it will corrode very rapidly at the unprotected spot (known as localised corrosion or pitting) because of the large cathode to anode ratio (corrosion rate is a function of current density). Oxidising types of inhibitors have additional problems in that they may depolarise the cathodic reaction and accelerate corrosion before they have passivated the entire anode area.

Cathodic inhibitors retard the cathodic process. There are three basic types of cathodic inhibitor:
Oxygen scavengers - these remove oxygen from the system and thus prevent it from depolarising the cathode. Sodium sulphite and hydrazine are two common scavengers: they are most effective in near neutral and slightly acid solutions, and are ineffective in strongly acid solutions where the primary cathodic reaction is hydrogen evolution. Sodium sulphite and hydrazine are used in closed systems, particularly boiler waters.
Hydrogen evolution poisons (ions of some of the heavy metals such as arsenic, antimony, bismuth) retard hydrogen polarisation i.e. they retard the reaction 2H+ + 2e -- H2. These inhibitors are useful in low pH solutions but are ineffective when the major cathode reaction is oxygen reduction. They are detrimental if the metal is susceptible to hydrogen embrittlement because they increase the transfer of hydrogen into the metal as opposed to letting it escape from the solution as a gas.

Insoluble films that form on the cathode and reduce its effective area, for example the addition of calcium bicarbonate to iron in neutral or slightly alkaline water, which is then converted to insoluble calcium carbonate.

Cathodic inhibitors are not dangerous in the same way as the anodic ones because they do not stimulate corrosion if present in sufficient quantity.

Oxidising or non-oxidising inhibitors are characterised by their ability to passivate the metal. In general non-oxidising inhibitors require the presence of dissolved oxygen in the liquid phase for the maintenance of the passive oxide film whereas dissolved oxygen is not necessary with oxidising inhibitors.

Some Soviet authors classify inhibitors as Type A to include film-forming types or Type B, which act by deactivating the medium by the removal of dissolved oxygen. Type A inhibitors are then subdivided into A (i) inhibitors that slow down corrosion without suppressing it completely and A (ii) inhibitors that provide full and lasting protection.

From the practical aspect a useful classification is perhaps one based on the concentration of inhibitor used. Generally inhibitors are used at low concentrations, say less than 50 ppm. The determining factor in the selection of the concentration used are the economics, disposal problems and the facilities available for monitoring the inhibitor concentration. To be fully effective all inhibitors require to be present at certain minimum concentrations. Not only is the initial concentration of importance but also the concentration in service. Inhibitor depletion occurs for a variety of reasons including its reaction with contaminants, the formation of protective films, windage losses in cooling towers, blow down in boilers and general leakages.

Inhibitor control can be effected by conventional methods of chemical analysis, inspection of test specimens or by instrumentation. The application of instrument methods is becoming of increasing importance particularly for large systems. Instrument techniques most widely used are based on the Linear Polarisation method and the Electrical Resistance method. These techniques have the advantage that readings from widely separated areas of the plant can be brought together at a central control point.

Considerations in the Design of a Chemical Injection System

Specific Gravity

Capacity

The main effect of the specific gravity of the liquid being sprayed is on the flow rate on the nozzle. Basically the velocity is affected which, in turn, affects the flow rate or capacity of the nozzle. The higher the density or specific gravity of the liquid, the slower the velocity through the nozzle, and thus the smaller flow rate. The following formula gives the relationship of the specific gravity to the nozzle capacity:

$$\text{CAPACITY (liquid sprayed)} = \text{CAPACITY (water)} \times \frac{1}{\sqrt{\text{S.G.}}}$$

In other words, the flow rate of a nozzle spraying a liquid other than water is the water flow rate of the nozzle divided by the square root of the specific gravity. Fig.1 shows a graph of the conversion factor versus the specific gravity. The conversion factor is merely the reciprocal of the square root of the specific gravity thus:

CAPACITY (liquid sprayed) = Convers ion Factor x CAPACITY (water)

It should be remembered that this conversion factor only accounts for the effect of the specific gravity on the capacity. It does not account for other factors such as the viscosity of the liquid.

Example: Find the capacity of a ¼U 8030 Veejet Nozzle spraying No. 1 fuel oil, specific gravity 0.80, at a pressure of 30psi.
Solution: The effect of viscosity in this case is negligible and thus only the specific gravity need be considered. From Fig.1 the conversion factor corresponding to a specific gravity of 0.80 is 1.12. The water capacity of the Veejet nozzle at 30 PSI is 2.6GPM. Thus:
Capacity of the nozzle spraying No.1 fuel oil is1.12 x 2.6 = 2.9 GPM.

This factor is important for nozzles where there is no whirling action to the spray i.e. Veejets, Flatjets, Solid stream nozzles. With the exception of extreme cases, the viscosity has negligible effect on the capacity of these nozzles and the only factor to consider to calculate nozzle capacity is the specific gravity of the fluid being sprayed.

Spray Angle

The effect of the specific gravity on spray angle is negligible. This is because the change in velocity due to the specific gravity also results in a change in the mass with the result that the momentum of the spray particles remains the same. Since the momentum remains the same, the same energy is present to produce the spray angle and hence it remains the same.

Distribution

It is not possible to predict the effect of specific gravity on the distribution with any accuracy. With no variation of momentum any change in distribution, if any should be slight and may be discounted. The important factors affecting spray angle and distribution are viscosity and surface tension of the liquid.
Full and Hollow cone nozzles:
With these nozzle types a decrease in specific gravity results in an increase in Capacity because the Mass (Inertia) of the liquid in the nozzle is decreased.

Viscosity

Viscosity is usually the most important factor to be considered since it usually has a decided effect on all of the spray characteristics.

The effect of viscosity on capacity will depend on the type of nozzle being used. On hollow cone nozzles where there is some whirling action present, the tendency is for higher viscosities to slow down this whirling and turbulence thereby causing an increase in capacity.

This shows that:

1. The effect of viscosity on capacity decreases with larger size nozzles.
2. The capacity decreases to a certain value and then levels off. The percentage increase at which the capacity levels is the percent increase in capacity due to the specific gravity of the oil.
3. The discontinuity of the curve at the 2.5 GPH rated capacity is due to a change in whirl chamber size. This shows that design factors other than the orifice and inlet size enter into the consideration of the effect of viscosity on capacity.

On flat type sprays and straight stream nozzles where there is no whirling action present, the effect of viscosity is less apparent. With these types of nozzle the capacity tends to decrease with increases in viscosity. This is due to the frictional effect of the liquid. If the nozzle is considered as a piece of pipe, the capacity drop is due to the frictional losses incurred by the liquid flowing through the length of pipe. If the nozzle is considered as a short length of pipe frictional losses are small.

Spray Angle

The effect of viscosity on spray angle is the same irrespective of nozzle type. Any increase in viscosity is followed by a corresponding decrease in spray angle. The smaller the capacity of the nozzle, the more the viscosity affects the spray angle of the nozzle. The effect of viscosity on the spray angle of the hollow cone and full cone types is more pronounced.

Minimum spraying pressure is the point at which the nozzle starts to operate satisfactorily. This is usually when the cone becomes symmetrical and the spray is falling straight with essentially a zero spray angle. Minimum spraying pressure decreases with increase in nozzle size showing that the viscosity has less effect with the larger nozzles.

Distribution

Distribution is also affected by viscosity. In the case of flat type sprays, the increase in viscosity usually brings heavy edges to the spray. The distribution may in some cases be improved by the use of higher pressures but generally the pressure necessary for practical improvement is so high as to be impractical. For hollow and full cone type nozzles, the distribution will be good once the minimum operating pressure of the nozzle is reached. Flat type spray nozzles operate at a much lower pressure than their equivalent hollow or full cone nozzles but their distribution may not be the best.

As yet, no formula has been reached from which the various effects of viscosity may be calculated. Viscosity is that property of a liquid that presents resistance to flow.
Absolute viscosity is the ratio of the shearing stress to the shearing rate. Its units in the metric system are dynes-sec per sq. cm. and its name is the "poise". The "centipoise" is 1/100th of a poise.

The "kinematic viscosity" is the absolute viscosity (in centipoises) divided by the density (in grams per cubic cm.) and its unit is the "Centistoke".
The Saybolt Viscosimeter is widely used for practical measurements of viscosity. It operates on the principal that the time for a known quantity of liquid to flow through a tube of known length and bore is proportional to the coefficient of viscosity.
Viscosity is quoted as Saybolt Seconds Universal (SSU) or Saybolt Seconds Fural (SSFO).
Table 1 shows a listing of common liquids and the viscosities.

Table 1

Viscosity

Liquid	Temp	Centipose	SSU
Water	21°C / 70°F	0.98	31.5
Motor Oils			
SAE 10	21°C / 70°F	57 to 105	300 to 525
SAE 20	21°C / 70°F	105 to 185	525 to 950
SAE 30	21°C / 70°F	185 to 290	950 to 1500
SAE 40	21°C / 70°F	290 to 340	1500 to 1800
SAE 50	21°C / 70°F	340 to 750	1800 to 3900
SAE 60	21°C / 70°F	750 to 1300	3900 to 7000
SAE 70	21°C / 70°F	1300 to 2000	7000 to 11000
Fuel Oils			
No. 1	21°C / 70°F	1.5 to 5.1	33 to 45
No. 2	21°C / 70°F	3.7 to 9.0	40 to 60
No. 3	21°C / 70°F	11	70 max
Kerosene	21°C / 70°F	1.935	
Gasolene	21°C / 70°F	0.82	

Effect of viscosity on particle size.
Increase in velocity increases particle size by a power factor in the range 0.17 to 0.2. On hollow and full cone nozzles this effect is increased because of the increase in flow rate with increase in velocity (same amount of swirl into more liquid results in less shear force per unit volume).

SURFACE TENSION

The main effect of surface tension is on the spray angle and the particle size of the spray.

The surface of a liquid tends to assume the smallest possible size and acts in this respect like a membrane under tension. Any portion of the liquid surface exerts a tension upon adjacent portions or upon other objects with which it is in contact. This force is in the plane of the surface and its amount per unit length is known as the surface tension. Its value for water is about 73 dynes per cm. at 70°F. Thus, if a line 1cm long is imagined on the surface of the water, the surface on either side of the line exerts a force of 73 dynes upon the surface on the other side.

Spray angle

The surface tension works at the web of the spray produced by a nozzle. The web of the spray is a solid sheet of liquid in front of the nozzle orifice from which the spray droplets break away. A high surface tension tends to pull this web together with a resulting smaller spray angle. A low surface tension allows this web to expand and a wider spray angle results. The effect of surface tension is more noticeable on the hollow cone and flat spray nozzles. With a full cone nozzle little or no web exists and the effect of surface tension on the spray angle is usually negligible. At present no formula exists to calculate the effect of surface tension on the spray angle.

Capacity

In all cases the effect of surface tension on capacity can be neglected.

Distribution

The effect of surface tension on nozzle distribution is varied. With hollow cone nozzles, when the surface tension is lowered below that of water, the cone becomes more concentrated with less of the fine off spray on the outer and inner parts of the cone. The distribution through radial segments will however remain the same. In the case of flat sprays a reduction in surface tension below that of water results in a shift in distribution. The tendency is for some of the liquid to shift out from the centre portion of the spray. This does not mean that the spray gets heavy edges; the shift is more gradual and extends all the way out to the edges.

Minimum spraying pressure

Since a lower surface tension produces a higher spray angle, it also allows the nozzle to be operated at a lower pressure. With liquids possessing a high surface tension, the minimum spraying pressure becomes very high.

Temperature

The temperature of the liquid being sprayed is of importance because of its effect on properties of the liquid which in turn affect the spray characteristics of the nozzle. Table 2 shows the results of the tests run on a nozzle spraying water at three different temperatures.

Table 2

Water Temperature	4°C / 40°F	21°C / 70°F	82°C / 180°F
Viscosity-Centipoises	1.55	0.98	0.35
Specific Gravity	1.00	0.998	0.970
Surface Tension Dynes/cm	75.0	72.6	62.2
Capacity-GPH @ 40psi	1.13	1.00	0.89
Spray Angle/ Pressure psi	51°/27	54°/25	64°/17

The decrease in capacity with increase in temperature is due to the decrease in viscosity of the water. The full effect of the change in viscosity is not shown, however, since any increase in temperature is accompanied by a corresponding decrease in specific gravity, which tends to increase the capacity and thus counteract the effect of the viscosity change. The increase in spray angle with increase in water temperature is due to the combined effects of the viscosity and surface tension of the water, both of which decrease with increases in temperature.

Temperature is more important with other liquids, such as oil, since the viscosity changes are much more rapid with changes of temperature.

Pressure Differential

This is the pressure drop across the nozzle and is the difference in injection pump pressure and the operating vessel or pipe pressure. Ideally, the pressure at the injection pump should be 100 PSI (7.03Kg/cm^2) higher than in the operating vessel or pipe.

Nozzle capacity varies with spraying pressure. In general, the relationship between capacity and pressure is as follows:

$$\frac{CAPACITY\ (Lit/\ min1)}{CAPACITY\ (\frac{Lit}{min2})} = \frac{kp/cm2}{kp/cm2}$$

Spray Atomization and Particle Size

Fine atomization is most easily obtained with air atomizing nozzles because compressed air is used to break up the liquid into fine particles. The higher the pressure the smaller the spray particles. Spray particle sizes become coarser as nozzle capacities, increase, spray angles become narrower as pressure decreases. The largest particles are obtained with the largest capacity full cone nozzles operating at the lowest pressure.

In general, to produce larger particles use:

1. larger size orifice and core slots
2. lower pressures
3. narrower spray angles

or some combination of these three factors. Solutions with lower viscosity and surface tensions characteristics tend to form larger particles.

To produce smaller particles use:

1. smaller size orifices and core slots
2. higher pressures
3. wider spray angles

or some combination of these three factors. Solutions with lower viscosity and surface tensions characteristics tend to form smaller particles.

Analysis of inhibitor distribution

An analysis of the flow and inhibitor distribution within the system may be carried out using the input data listed below.

Film Maintenance (F) -- $cm^3/m^2/day$
Chemical Addition Rate (C) -- cm^3/day
PPM Dosage (P) -- PPM by volume
Rate of Flow (R) -- m^3/day
Velocity of Flow (V) -- m/sec.
Internal Diameter of Pipeline (D) -- cm
Length of Pipeline (L) -- km
Area of internal surface (A) -- m^2

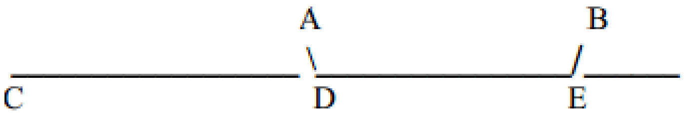
Relationships between these input data parameters are:
A = 10` D.L. -- 1
C = F.A. ($cm^3/day = cm^2/m^2/day/m^2$) ----------- 2
C = P.R. ($cm^3/day = ppm/m^3/day$) ------------- 3
R = 6.786.D2.V. ($6.786.cm^2.m/sec$) ----------- 4

Basic concepts of the analysis are as follows:

1. The Chemical additions, rate is proportional to the surface area to be protected.
2. The minimum values of Film Maintenance is a constant for a common source system and a particular inhibitor.

3. The Distribution Factor (E) for a section of the system is the area of internal surface in the system per unit of flow.
4. The total surface to be protected is equal to he summed values of E. = Σ
5. PPM Dosage (P) = Film Maintenance (F) x Σ

The following examples may serve to illustrate the principle:



The diagram represents a typical injection system.
A and B are well heads. C-E represents a main header pipe, which is being fed via the wellhead flow lines A-D and B-E. Physical dimensions of the pipes and flow data are given in Table 1.

Pipe Run	L	D	R
C-D	1.0	30.5	10,000
D-A	2.0	20.3	6,000
D-E	4.0	30.5	4,000
E-B	2.0	2.0	4,000

Table 1

Using the data in Table 1 calculate values for A (= 10. 11. D.L.)

Velocity (V) = $\left(\frac{R}{D2 \times 6.786}\right)$, and the Distribution Factor (E).

Calculated values for the example are given in Table 2.

Pipe Run	A	V	E	∑
C-D	458	1.6	0.096	0.096
D-A	1275	2.1	0.213	0.309
D-E	2833	0.6	0.958	1.054
E-B	1275	1.4	0.319	1.373

The distribution of inhibitor in the system should favour branch E-B with injection totally at point C. To determine the most effective distribution of inhibitor the following procedure may be used:

The distribution of inhibitor in the system should favour branch E-B with injection totally at point C. To determine the most effective distribution of inhibitor the following procedure may be used:

A Adjust the dosage at point C until satisfactory monitoring results are obtained at wellhead A. Let us suppose this is 6 ppm, which is value P for branch D-A

B Calculate the value of F for the system
P - 6.00 and = 0.309. Therefore F is 19.4.

C Use this value of F to calculate P for the rest of the system.

$$P = 19.4 \text{ x. } \Sigma$$

P is then calculated to give the same degree of protection to other parts of the system.

i.e. E to B is 1.373

Therefore P = 19.4 x 1.373 - 26.6 ppm

D Plan supplementary injection points based on the calculated values of P. We have 600 ppm required to protect up to wellhead A and 26.6 ppm required to protect up to wellhead B. Introducing a supplementary injection point at D feeding into feeder line C-E we can supplement the 6.00 ppm at C with 20.6 ppm at D.

Calculated savings based on this analysis of inhibitor distribution:

Increasing dosage at C until protection was obtained at wellhead B would require about 26.6 ppm based on the total flow.
C = P x R, so C = 26.6 x 10,000 cm^3 /day or 1.28 drums/day.

Using only 6 ppm at C and 20.6 ppm at D would require
(6.0 x 10,000) + (20.6 x 4000) = 60,000 + 82,400 cm3/day = 0.68 drums per day.

Savings are thus 0.6 drums/day or 47%.

Limitations of Distribution Analysis

The severity and type of corrosion in any system and the effectiveness of its control by a given inhibitor depend on a large number of interacting variables. Such variables include:

- System design
- System materials of construction
- Flow pattern, Flow velocities and pressures
- Chemical and physical flow composition
- Chemical and physical properties of the inhibitor
- Changes in corrosivity can occur through the system due to the addition or removal of elements of the fluid or gas affecting its corrosivity
- Flow velocity has an effect on the chemical and physical attachment of a corrosion inhibitor, a metal surface, in addition to its effect on film stability. Flow velocity, in multiple phase flow in particular, is the controlling factor for erosion effects. This applies to entrained particles and gas bubbles. Some inhibitors may have concentration and solubility limits, which may cause undesirable side effects at high dosage