

Corrosion Inhibitor Encapsulation for Enhanced Chemical Efficiency and Performance

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ABSTRACT

Liquid corrosion inhibitor (CI) package injection is one of the most cost-effective solutions and commonly applied methods to control internal corrosion and prevent corrosion failures of carbon steel pipelines in the oil and gas industry. However, due to the amphiphilic nature of CIs, a significant fraction of the injected CI is lost into the oil phase through partitioning, dramatically decreasing the efficiency of CIs due to lowered CI concentration in the water phase. To enhance CI efficiency, a novel CI encapsulation technology was developed to bypass the oil phase and deliver inhibitors directly to the water phase.

In this study, commercial CI packages as well as custom CI blends were encapsulated with water soluble matrix materials into microsphere morphology via spray drying technique. The stability of the encapsulated CIs in crude oils as well as synthetic oil was evaluated via weight loss measurement and the payload of the encapsulated CIs was estimated via solubility study in polar solvents. Partitioning behavior of encapsulated CI in an oil/water two phase system was investigated using methyl orange CI residual measurement method. The corrosion inhibition performance of encapsulated CIs in sweet aqueous corrosion environment was evaluated and compared with conventional liquid CIs through

electrochemical corrosion tests. Due to minimized CI loss in oil phase, encapsulated CIs demonstrated superior corrosion inhibition efficiency and performance to commercial liquid CIs in an oil/water two phase system.

Key words: corrosion inhibitor, encapsulation, sweet corrosion, partitioning, inhibition performance

INTRODUCTION

Corrosion of pipelines made of carbon steel and exposed to wet hydrocarbons containing CO_2 and H_2S is a common but serious problem encountered in petroleum industry and its occurrence causes enormous expense due to production downtime, accidental injuries, and replacement costs. Control and prevent corrosion using chemical treatment (e.g. corrosion inhibitor injection) is one of the most cost-effective solutions and commonly practiced methods to prevent corrosion failures in pipelines in oil and gas industry [1]. Generally speaking, the active corrosion inhibitor (CI) components in commercial CI packages are usually organic, nitrogen-based surfactants such as amines, imidazoline and its derivatives. Due to the amphiphilic nature of surfactants, a good fraction of the injected CI will inevitably go into the oil phase through partitioning and to the oil/water interface [2-5]. It is important to emphasize that CI inhibition efficiency is dependent on its capability to be present in the water phase to a great extent since corrosion happens only when acidic water is in contact with the steel surface. As a result, CI partitioning into the oil phase can significantly reduce the effectiveness of the inhibitors due to lowered CI concentration in the water phase [2]. Therefore, to enhance the efficiency of CI treatment in controlling corrosion of carbon steel pipelines, there is a need to minimize CI loss into the oil phase and maximize the amount of injected CI in the water phase. To this end, a novel CI encapsulation concept was developed and demonstrated to deliver inhibitors directly to the brine phase, resulting in significantly enhanced inhibition efficiency [6-7]. Figure 1 shows schematically the encapsulated CI concept as compared to the conventional direct CI injection where a large fraction of CI was lost into the oil phase.

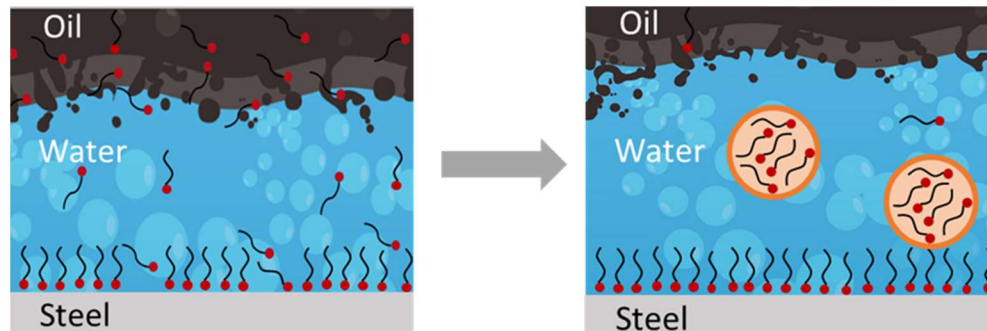


Figure 1: Schematic illustration of the encapsulated CI concept (right) for directly CI delivery to the water phase, as compared to the conventional direct CI injection (left) where CI loss into the oil phase is inevitable.

A suitable and economical encapsulation technology for commercial liquid CI packages was developed in this study. Two commercial CI packages and several solvent free, custom CI blends were successfully encapsulated with different water soluble matrix materials into microsphere morphology via spray drying technique. The stability of the encapsulated CI in oil at ambient pressure, as well as under pressure, was evaluated via weight loss measurement. The payload of the encapsulated CIs was estimated via solubility study in polar solvents. Partitioning behavior of encapsulated CI in an oil/water two phase system was investigated using methyl orange CI residual measurement method. The corrosion inhibition performance of encapsulated CIs in sweet aqueous corrosion environment was evaluated and compared with conventional liquid CIs through electrochemical corrosion tests.

EXPERIMENTAL PROCEDURE

Two fully formulated, commercially available corrosion inhibitor packages (CI package-A and CI package-B) and several custom blends of common corrosion inhibitors were evaluated for encapsulation. The encapsulation matrices and their suppliers are listed below in Table 1. All materials are fully soluble in water and were used as received. Table 2 lists the pure CIs used in custom blends without solvent for encapsulation.

Table 1. Encapsulation Matrices

Material	Grade	Supplier
Maltodextrin	Maltrin M100	Grain Processing Corporation [†]
Gelatin, porcine	300 Bloom, 40 mesh	Custom Collagen [†]
ZeMac	E60	Vertellus [†]
Methyl cellulose	SG A150	Dow Chemical [†]
Sodium hexametaphosphate		Calgon [†]
Gum acacia		Spectrum [†]
Fish Gelatin	HMWD	Kenny & Ross [†]
Starch	HiCap 100	Ingredion [†]
Poly(vinyl alcohol)	80% hydrolyzed	Sigma-Aldrich [†] (Supplier X)
D-Mannitol		

Table 2. List of pure corrosion inhibitors used in custom blends for encapsulation

CI Name	Product Name	Supplier
DDA	Dodecylamine	Acros Organics [†]
BC12	Benzyldimethyldodecylammonium chloride	Supplier X (See Table 1)
BC16	Benzyldimethyldodecylammonium chloride	
DDT	Dodecanethiol	
MCE	2-Mercaptoethanol	

The corrosion inhibitors were encapsulated in microsphere morphology using spray drying. Formulations and spray drying conditions are provided in Table 3. Aqueous solutions and suspensions were prepared by dissolving the matrix material into water, followed by dispersion of the corrosion inhibitor to form a homogeneous solution for spray drying. The exception was sample P36, which was formulated with methanol. The solutions were spray dried using a Pro-C-epT 4M8-TriX[†] laboratory spray dryer. The solution was atomized using a 0.4 mm bifluid nozzle with a nozzle pressure of 3.1 bar, fed at a rate of approximately 5-6 g/min. Air speed for all runs was set to 0.3 m³/min. The air inlet, chamber, and outlet temperatures are included in Table 3. These were varied based on the material and objective of the run. For example, most aqueous formulations were spray dried with an inlet temperature of 160-170 °C to adequately dry off the water. One of the gelatin formulations, P12, and formulation in methanol, P36, were spray dried at lower temperatures in an effort to preserve any volatiles carried over from the corrosion inhibitor formulations. Of additional note, the solutions prepared with porcine gelatin were heated to, and maintained at, 50 °C to prevent gelation.

[†]Trade name.

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Table 3. Formulation and spray drying condition for corrosion inhibitor microencapsulation

Sample #	Matrix	Matrix Amt (g)	Corrosion Inhibitor (CI)	CI Amt (g)	CI/(CI+matrix) [#]	Water (g)	Additional Excipient	Amt (g)	Air Inlet (°C)	Chamber (°C)	Outlet (°C)
P11	Maltodextrin	15.75	package A	70	82%	89.25			170	67.9	62.3
P12	Gelatin	24	package A	134	85%	215			60	26.5	32.2
P13	Mannitol	14	package A	60	81%	126			160	70	63
P14	Methyl cellulose	3.5	package A	60	94%	136.5			160	69.6	63.7
P23	Gelatin	12	package A	134	92%	215	Na ₂ SO ₄	12	160	62.2	62
P22	Methyl cellulose	8.5	package B	60	88%	331.5			160	50.7	53.2
P25	Maltodextrin	15.75	package B	70	82%	89.25			170	40.4	36.6
P27	Maltodextrin	18	package B	40	69%	96			170	38.2	41.9
P28	Maltodextrin	17	package B	20	54%	80			170	43.4	40.5
P31	Maltodextrin	12	package B	8.00	40%	100			170	50.5	40.4
P32	Gelatin	12	package B	8.00	40%	280			170	57.9	46.7
P33	Polyphosphate	12	package B	8.00	40%	200			170	57.8	45.5
P34	Gum Acacia	12	package B	8.00	40%	200			170	58.7	40.7
P35	Fish Gelatin	12	package B	8.00	40%	188			160	47.7	39
P36	ZeMac	12	package B	8.00	40%	100			80	34.2	29.2
P37	Gelatin	3.75	package B	8.75	70%	48.75			150	52	45.2
P39	Sodium alginate	1	package B	5.00	83%	69	Starch	4	120	35	32
P40	Poly(vinyl alcohol)	15	package B	15.00	50%	135			120	36.2	32.4
P43	Gelatin	10	BC12:BC16:DDA*	10.00	50%	190	SDS	0.1	140	55.8	52.8
P44	Gelatin	10	BC12:BC16:DDA*	4.29	30%	190	SDS	0.1	140	80.4	66.5
P51	Gelatin	17.5	BC12:BC16:DDT*	17.50	50%	300	SDS	0.18	170	75.6	68.6
P52	Gelatin	17.5	BC12:BC16:DDA*	17.50	50%	300	SDS	0.18	170	82	72.7
P53	Gelatin	17.5	BC12:BC16:MCE*	17.50	50%	300	SDS	0.18	180	85.8	72.9

[#]CI/(CI+matrix) before spray drying, different from payload which is the concentration of active CIs in the capsule

*4:3:3 ratio of components listed.

SDS: Sodium dodecyl sulfate

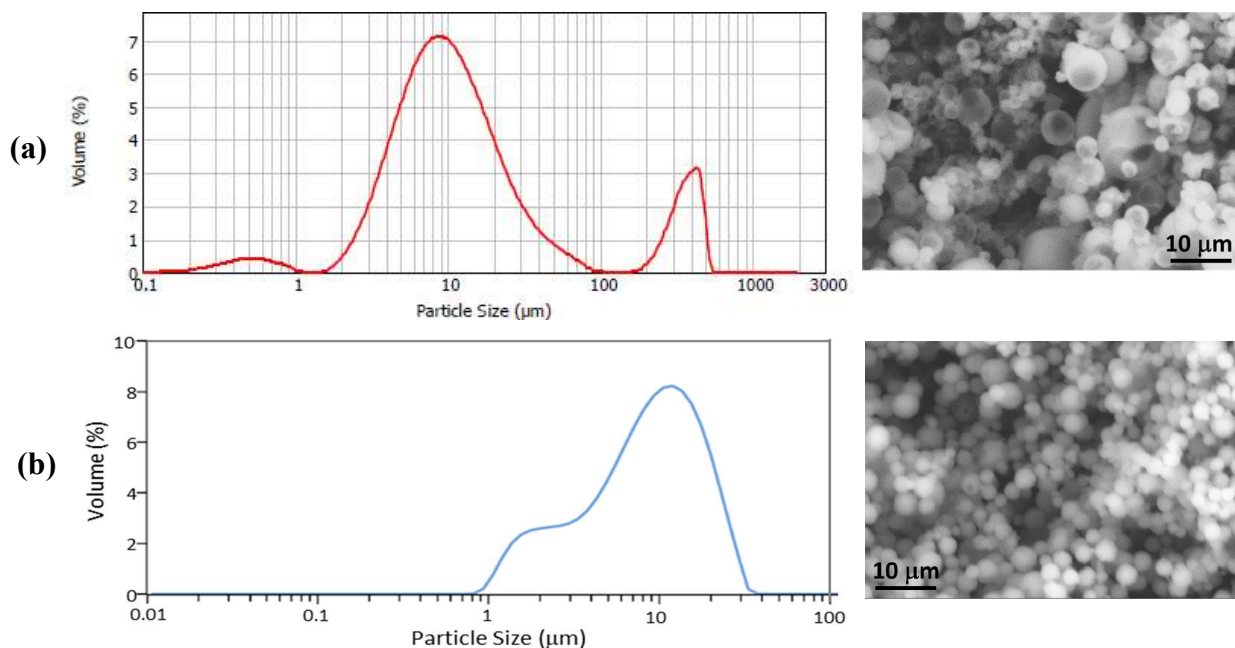


Figure 2: Particle size analysis and scanning electron micrograph of formulation (a) P28 and (b) P36

Laser diffraction particle size analysis of the collected dry powders of P28 and P36 reported primary average particle size in the range of 5 to 25 μm , as shown in Figure 2. The secondary smaller peak observed over 400 μm for P28 is confirmed to be agglomeration of the smaller particles that failed to break apart during the sizing. Secondary scanning electron micrographs of two samples, shown in Figure 2, confirm the small size and spherical morphology.

The stability of the matrix materials in crude oil or model oil selected for CI encapsulation was tested through solubility and weight loss measurement. For each test, 0.2 g of matrix was added in 2.5 g of oil. Then the mixture was stirred with vortex mixture for 0.5 hr and kept at room temperature overnight. The matrix material was then filtered out from the solution mixture with disposable filter funnel, washed with heptane, and dried under vacuum. The final weight of the matrix material was then measured and the weight loss of the material in oil was calculated. The stability of the encapsulated CI in oil was tested following the same aforementioned procedure.

The stability of the encapsulated CI in PAO4 (Poly Alpha Olefin, Synthetic group IV basestock) model oil under high hydrostatic pressure was tested in the lab. The testing procedure is as following: 1) put 1.3 g encapsulated CI in 20 ml PAO4 in a stainless steel pressure reactor, 2) stir the mixture with vortex mixture for 0.5 hr, 3) keep the solution mixture under high nitrogen gas pressure for certain period, 4) release the pressure in the pressure reactor and filter out the encapsulated CI capsules in the solution mixture with disposable filter funnel and wash with heptane, 5) dry the filtered out capsules under vacuum and measure the weight loss.

The payload (fraction of the active CI components in the encapsulated CI) of the encapsulated CI was estimated via weight loss measurement in toluene and xylene as the matrix materials are stable in these solvents. The testing procedure is similar to the aforementioned procedure for encapsulated CI stability tests, except that toluene or xylene was used instead of oil.

CI partitioning tests were conducted on encapsulated CI with different matrix materials. For each test, 20 mg of either solid encapsulated CI, 20 mg of liquid neat CI, or solid encapsulation matrix material without CI (blank test) was added to a water and oil mixture of 1 L in total volume. The water-oil mixture was made of a 1 wt.% NaCl solution with 80 vol.%, balancing with a crude oil. The fluid was mixed in a beaker by a stir bar with different rotating speeds (either 100 rpm, 200 rpm, or 600 rpm). While 100 rpm and 200 rpm tests mimic stratified flow condition with a clear oil and water interface; 600 rpm test mimics more violent flow patterns that oil and water are fully mixed. Mixing was continued for an hour for each test. After that, mixing was stopped and oil and water started to separate. Samples from water phase were then withdrawn, and CI residuals were measured by methyl orange method [8].

The inhibition performance of encapsulated CI as compared to the directly injected CI solution in an oil and water system was evaluated using electrochemical corrosion tests. Corrosion tests were conducted in 3 liter cylindrical corrosion glass cell filled with 1 wt.% NaCl solution at 80 vol.% and 20 vol.% crude oil. A. Magnetic stirring at a speed of 100 rpm was used to provide an even temperature distribution and good mixing during each experiment. All the tests were conducted at room temperature and atmospheric pressure with continuous CO_2 purging. Prior to each test, the brine solution was purged with N_2 for 1 - 2 hrs in order to deoxygenate, then CO_2 gas was bubbled into the solution for about 2-4 hours to ensure CO_2 saturation. The solution pH was then adjusted to the targeted pH by adding appropriate amount of either hydrogen chloride or sodium bicarbonate. The pH of the brine solution was monitored during the course of the test by a pH probe inserted into the cell and a variation of ± 0.2 pH unit to the targeted pH was achieved for all the tests.

Electrochemical corrosion tests were undertaken using a standard three electrode arrangement, using a platinum wire as counter electrode, a saturated calomel electrode as the reference electrode, and a cylindrical working electrode made from X60 carbon steel. Before each tests, the working electrode (WE) was prepared by wet grinding to a 600-grit sand paper finish, rinsed with DI water, methanol and acetone, then it was blow dried with nitrogen gas. The dimensions of the electrode were then measured to