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Corrosion inhibition of zinc by calcium exchanged beidellite clay mineral: A new smart corrosion inhibitor

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ABSTRACT

The corrosion inhibition performances of zinc immersed in 0.1 M NaCl solution with and without $CaCl_2$, Na^+ and Ca^{2+} exchanged beidellite (BDT) clay mineral picked up from Agadir bassin (Morocco) was studiedby potentiodynamic measurements and electrochemical impedance spectroscopy. The chemical and microanalysis of Na^+-BDT and Ca^{2+}-BDT by different techniques reveal basal distances of clays, of about 1.22 and 1.48 nm respectively, consistent with the saturation of beidellite interlayer spaces with Na^+ and Ca^{2+} ions surrounded by one and two equivalent layers of water respectively. EIS results and surface analysis show that Ca^{2+}-BDT acts as a smart inhibitor on zinc surface by modifying the physicochemical parameters of electrolyte near the surface. The exchange reaction in BDT involves the concentration decrease or the "suppression" of Na^+, CO_3^{2-} and Cl^- ions near the zinc surface.

1. Introduction

Zinc is an important structural metal extensively used in many applications. Due to its good corrosion resistance and relatively low price [1], the most prominent and well known application of zinc is its use as sacrificial anode in the galvanized steel. In general, zinc based coatings corrode on the order of 100 times slower than cold rolled steel due to the inhibiting or barrier effect of zinc-based corrosion products [2]. According to the composition of environments, zincite (ZnO) and zinc hydroxide ($Zn(OH)_2$) are often the first compounds formed but they are rapidly transformed in to hydrozincite ($Zn_5(CO_3)_2\,(OH)_6 \cdot H_2O$), or simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$), that formed the whit rust of zinc [3–5]. In very aggressive media, such as concentrated sodium chloride solution, the growth rate of these compounds is accelerated by the presence of very high amounts of chloride as well as of sodium ions [6].

Thus, the protection and life time of zinc materials could be further reinforced and lengthened respectively by coatings containing corrosion inhibitors. Chromate was for a long time the most efficient and used inhibitor. Nevertheless, due to its high toxicity and hazards both to the environment [7] and to human health, with known carcinogenic effects [8], today's eco-awareness motivates for the search for an environmental friendly corrosion inhibitors to protect zinc. In this respect, cations such as Ce^{3+} [9], Mg^{2+} [6], Ca^{2+} [10–12], or other organic anions such as carboxylates [13], are considered as alternative potential non-toxic safe inhibitors. Nevertheless, their use as salts directly in corrosive media or in coatings may allow their quick consumption while their insertion within host materials provides their controllable progressive release on the surface. Thus, their released amount would depend on the severity of the environment which would permit to long term anticorrosive protection to be improved, as observed for the steel protection [14]. Amongst hosts materials considered, there are silicon gels exchanged with Ca^{2+} [15], Layer Double Hydroxides (LDHs) known as containers of inhibitors for corrosion protection of carbon steel [16] and clay minerals, especially the family of smectites, characterized by their cationic exchange and adsorption properties [17,18]. In this respect, we already achieved the development of corrosion inhibitor based on chitosan-heptanoate modified natural beidellite taken from Agadir bassin (Morocco) which showed corrosion inhibition better than the commercially available triphosphate aluminum (TPA) [19]. Despite the non-toxic and "green" properties of this formulation, the purification and synthesis of modified-clay minerals remain relatively long and sometimes expensive.

So, the present work aims at on one hand the development of corrosion inhibitor based on Ca^{2+} exchanged beidellite, which is simpler than the beforehand mentioned, and on the other hand the study of its corrosion inhibition performances to protect zinc.

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2. Experimental

2.1. Preparations and characterizations

The raw clay, labeled BDT, was picked up from the region of western high Atlas basin of Agadir (Morocco). It was already characterized in details by Bouna et al. [20]. Homoionic sodium beidellite, labeled Na^+-BDT, having particles sizes ‹2 μm, was first isolated from the raw clay, according to the procedure we described elsewhere [20,21], and thereafter used to prepare different materials involved in the present study. Detailed characterizations of Na^+-BDT fine fraction were carried out by Bouna et al. [20], who found that it was made up of 93% of beidellite, and 7% of kaolinite. Its cationic exchange capacity (CEC), BET specific surface area and total pore volume were assessed to be around 59.7 meq $(100\ g)^{-1}$, 82.2 $m^2\ g^{-1}$ and 0.136 $cm^3\ g^{-1}$ respectively. The formula of beidellite was determined, after subtraction of kaolinite contribution, to be $(Si_{7.51}Al_{0.49})(Al_{2.99}Fe_{0.68}Mg_{0.33})(Ca_{0.03}Na_{0.54}Mg_{0.11})O_{20}(OH)_4$ [20].

Aqueous solutions were prepared from chemicals of analytical reagents grade: NaCl (99.5 wt.%), $Ca(NO_3)_2$ (99 wt.%), $CaCl_2$ (99 wt.%), HCl (35 wt.%) and $AgNO_3$ (99 wt.%). All these chemical products were purchased from Aldrich and were used as received without any further purification. Pure Zinc plates (99.99 wt.%) were provided by Goodfellow, France.

The Ca^{2+}-exchanged beidellite, noted Ca^{2+}-BDT, was simply prepared by ion exchange reaction. 5 g of Na^+-BDT was added to calcium nitrate $Ca(NO_3)_2$ solution (1 M), the mixture was kept under stirring for 12 h. The clay mineral fraction was recovered by centrifugation at 3500 rpm (604×g) using a Hermle Z300 device (Labortechnik, wehingen, Germany) for 40 min. This operation was thrice repeated to assure complete exchange of Na^+ interlayer cations with Ca^{2+}. The Ca^{2+}-BDT was recovered by repetitive washing with distilled water, dried at 353 K and then stocked for following uses.

The different exchanged beidellite samples, Na^+-BDT and Ca^{2+}-BDT, and the corrosion products were characterized by X-ray diffraction (XRD) using Philips XPert Pro diffractometer equipped with copper anticathode ($\lambda_{K\alpha}$ = 1.5418 Å). Microstructural observations and elemental analysis of the different materials were carried out by Field Emission Scanning Electron Microscopy (FE-SEM JEOL J7600F) equipped with Energy Dispersion Spectrometer (EDS).

The dehydratation/hydratation processes of the different clays were studied by Thermogravimetry (TG) coupled to controlled humidity gas generator (CHGG) by using the following cycle:

(a) heating from 35 to 150 °C to get the sample dehydrated and then cooling to 35 °C under dry air for one hour (phase I),
(b) hydration in air moist whose relative humidity (RH) is around 60% at 35 °C (phase II),
(c) second dehydration under dry air by heating up to 150 °C followed by cooling at35 °C (phase III).

Finally, the kinetic of Ca^{2+} release from Ca^{2+}-BDT was measured in a batch reactor by dispersing 1 g of Ca^{2+}-BDT in 500 ml of 0.1 M NaCl solution at 25 °C. The concentration of Ca^{2+}, released by ion exchange from Ca^{2+}-BDT, was assessed by atomic absorption spectroscopy: the analysis was performed on aliquots of 5 ml of supernatant taken from mixture at different time intervals. The spectrophotometer used was of type Perkin Elmer A. Analyst 100.

2.2. Electrochemical measurements

Square plates of pure zinc were used as working electrodes (2.27 cm^2). They were first grinded with silicon carbide (SiC) abrasive paper and there after polished with silica suspension (particle size 30 nm) until their surfaces got mirror aspect. Before electrochemical measurements, metallic samples surfaces were cleaned with ethanol and dried under hot air flow. 0.1 g of clayey material dispersion was mixed in 70 mL of electrolyte in cell, which flocculates under NaCl salt effect to form a layer on the zinc surface by sedimentation as in a same way reported by Jeannin et al. in the case of carbon steel [22].

In order to evaluate the usefulness of Ca^{2+} intercalation in beidellite, electrochemical test was also performed by introducing an amount of $CaCl_2$ equivalent to 1 CEC of beidellite.

Electrochemical experiments were carried out in a classical three electrode glass cell in aerated NaCl 0.1 M electrolyte: the horizontal working electrode was faced to a platinum grid used as counter electrode whereas KCl-saturated calomel electrode (SCE) was used as a reference electrode.

The measurements were carried out by using a potentiostat VersaSTAT4 monitored with software VersaStudio.

The following experimental sequence was used:

(a) measurements of the corrosion potential (E_{corr}),
(b) measurements of the electrochemical impedance spectrum from 100 kHz to 10 mHz with a 10 mV amplitude, every 2 h for a duration of 20 h to verify the system stability.

Anodic and cathodic polarization curves were recorded independently after 20 h of immersion in NaCl 0.1 M with a scan rate of 1 mV s^{-1} respectively from E_{corr} to E_{corr} +1 V and E_{corr} to E_{corr} −0.7 V. The impedance data were analyzed using the ZSimpWin software, using non-linear least squares fitting routine [23].

3. Results

3.1. Characterizations of clay materials

In the Fig. 1, the XRD pattern of Na^+-BDT sample reveals a well resolved (001) reflection centered at a basal spacing d_{001}at 1.22 nm, corresponding to an interlayer space of clay mineral containing a monolayer of water molecules surrounding Na^+ [24].

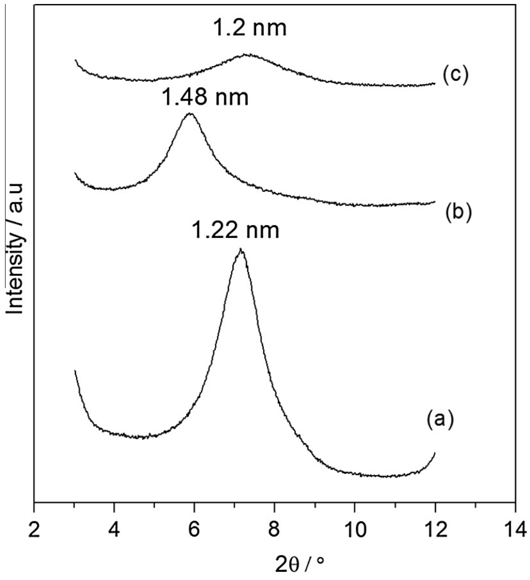

Fig. 1. XRD patterns of starting homoionic beidellite: (a) Na^+-BDT and (b) Ca^{2+}-BDT. The X-ray diagram (c) corresponds to the typical one recorded after ion exchange of Ca^{2+} by Na^+. (The basal distances corresponding to (001) reflexion are noted in nanometers).