

Inorganic–Organic Hybrid Molecular Ribbons Based on Chelating/
Bridging, “Pincer” Tetrakisphosphonates, and Alkaline-Earth Metals

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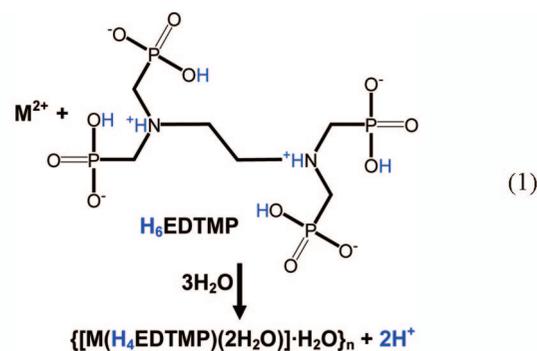
ABSTRACT: Syntheses and structures of alkaline earth metal ions and EDTMP, ethylenediamine-*tetrakis*(methylenephosphonate), are reported. The isostructural Ca^{2+} and Sr^{2+} analogs have 1D topologies, with EDTMP acting as both chelating and bridging ligand. The M-EDTMP compounds act as Fe-oxide removers from corroded surfaces.

The renaissance of metal phosphonate chemistry is witnessed by numerous significant publications that originate from several research groups around the world. Apart from “curiosity-driven”, basic research, metal phosphonates have found important applications in medicine¹ (e.g., palliation of metastatic bone cancer, antiresorption agents, osteoarthritis drugs, etc.), water treatment² (extraction of metals, mineral scale inhibition, corrosion control), gas storage and capture,³ dentistry⁴ (adhesives in dental composites), and dispersion technology⁵ (rheology modification). On the other hand, alkaline-earth metal ions, in particular Ca^{2+} and Sr^{2+} , play an important role in bone mineral formation and Ca^{2+} metabolism.⁶ Therefore, the study of interactions between alkaline-earth metals and phosphonates presents a fruitful area of research that has repercussions in several front-line disciplines.

In this communication, we report syntheses, structural characterization and some functional properties of alkaline-earth metal tetrakisphosphonate materials of the general formulas $\{M[(\text{EDTMP})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ ($M = \text{Ca}^{2+}$ (1), Sr^{2+} (2)) possessing 1D topologies and an unprecedented EDTMP chelating/bridging coordination mode. Iron oxide dissolution mediated by these M-EDTMP materials ($M = \text{Ca}^{2+}$ and Sr^{2+}) is also reported. To the best of our knowledge, this is the first use of phosphonates for iron oxide dissolution.

EDTMP is a tetrakisphosphonic acid that can potentially dissociate its 8 protons (two H^+ from four $-\text{PO}_3\text{H}_2$) depending on solution pH (see the Supporting Information for speciation curves).⁷ The basic N groups remain protonated up to pH of ~ 10 . Therefore, EDTMP can be described as a “zwitter-ionic” ligand. At pH 4, each phosphonate group is monodeprotonated, thus EDTMP possesses an overall “-2” charge. It is therefore ideal for the construction of divalent metal phosphonate frameworks based on simple charge neutralization principles. Thus, reactions of water-soluble M^{2+} ($\text{M}^{2+} = \text{Mg}^{2+}$, Ca^{2+} , Sr^{2+} , Ba^{2+}) inorganic salts with EDTMP in acidic pH's yield extended coordination polymers (see reaction scheme below and the Supporting Information).⁸ All syntheses produce single-phase products based on powder XRD. In the reaction scheme, proton content is highlighted in blue.

The structures of $(\text{NH}_4)_2(\text{EDTMP})$, **1**, and **2** have been determined by single-crystal X-ray crystallography.⁹ In the structure of $(\text{NH}_4)_2(\text{EDTMP})$, EDTMP exists as a discrete dianion, neutralized by two NH_4^+ ions (Figure 1, upper). The whole 2D layered structure is stabilized by hydrogen bonds between the $-\text{P}=\text{O}$ and $-\text{P}-\text{O}^-$ groups and the NH_4^+ cations or the protonated N atom (see the Supporting Information). Other structural features in $(\text{NH}_4)_2(\text{EDTMP})$ compare well with those of $\text{EDTMP} \cdot 2\text{H}_2\text{O}$.¹⁰



The crystal structures of the Ca(Sr)-EDTMP frameworks reveal extended, 1D coordination polymers with EDTMP^{2-} acting as both chelating and bridging ligand, Figure 1, middle and lower. There are some interesting features in these structures that warrant some attention. The $-\text{PO}_3\text{H}^-$ group coordinates to Sr^{2+} through only one of its three oxygens. This is in contrast to several literature examples that demonstrate the strong propensity of the $-\text{PO}_3\text{H}^-$ group to bridge two or more metal centers. Two $-\text{PO}_3\text{H}^-$ groups, one from each N, form an 11-membered chelate ring with Sr^{2+} . The same function occurs on the other side of the $-\text{CH}_2\text{CH}_2-$ linker that renders the whole tetrakisphosphonate a bridge between two Sr^{2+} centers. Thus, one can envision the 1D polymer as a ribbon in a “wavelike” motion composed of Sr-EDTMP-Sr dimers, see Figure 2. To the best of our knowledge, this coordination mode of EDTMP is unprecedented.

The Sr^{2+} is located in a slightly distorted octahedral environment shaped by four equatorial phosphonate oxygens and two axial H_2O molecules trans to each other.

The $\text{Sr}-\text{O}_{(\text{p})}$ bond distances are 2.4686(18) and 2.4884(16) Å, whereas the $\text{Sr}-\text{O}_{\text{water}}$ bond distance is 2.521(2) Å. The water of crystallization rests above a plane formed by four phosphonate oxygens. However, the H_2O molecule forms hydrogen bonds with from the “wire” above, with two protonated phosphonic acid moieties ($-\text{P}-\text{O}_5-\text{H}$) and with two phosphoryl oxygens ($-\text{P}=\text{O}_1$). The specific bridging mode of EDTMP observed in the structure of Ca(Sr)-EDTMP causes the ligand to acquire a strained position. Thus, the $\text{H}_2\text{O}-\text{Sr}-\text{OH}_2$ axial vectors in the dimeric “unit” are not aligned, but form a dihedral angle of 48.49°. Very few metal-EDTMP compounds have been reported with metal ions such as Eu^{3+} , Pb^{2+} , and Zn^{2+} .¹¹ The coordination mode of EDTMP is distinctly different in these materials.

Chemical cleaning of corroded steel surfaces is an important technological field of great industrial and economical significance.¹² Reported methods include use of polycarboxylate ligands and derivatives.¹² In our experiments in situ corroded carbon steel surfaces were used as specimens for iron oxide removal.¹³

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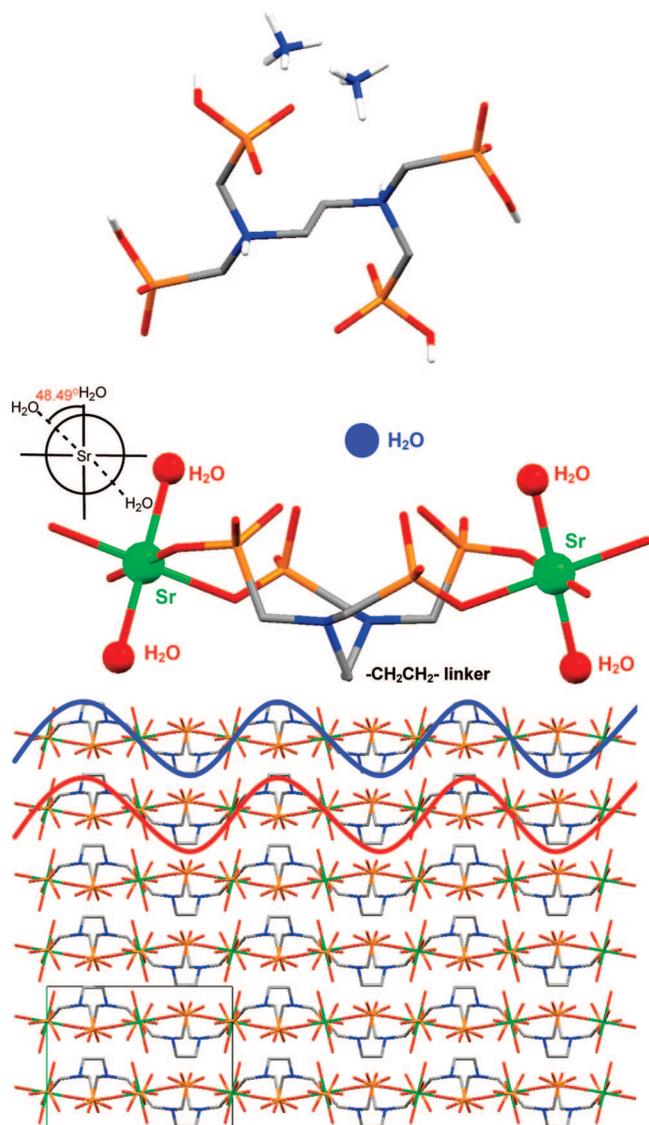


Figure 1. Structure of the EDTMP backbone and NH_4^+ cations in the structure of $(\text{NH}_4)_2(\text{EDTMP})$ (upper). Structure of the “Sr-EDTMP-Sr” dimer (middle), viewed along the $-\text{C}-\text{C}-$ bond vector. The water molecule of crystallization is shown as a blue sphere “resting” on the cavity created by oxygen atoms from four phosphonate groups. 1D “ribbons” viewed along the a -axis (lower). Color codes: C, gray; N, blue; O, red; P, orange; Sr, green; H, white.

The action of EDTMP (no metals added) and M-EDTMP ($\text{M} = \text{Ca}^{2+}, \text{Sr}^{2+}$) were studied and compared to the “control” (no additives). Quantification of corrosion rates (CR) by an established method¹³ (see caption of Figure 3) is indicative of the ability of a certain additive to protect a corroding surface. When CR is lower than that for the control, corrosion is inhibited.

When CR is higher than the control, base metal corrosion/loss (carbon steel in this case) occurs. These results must be combined with visual examination of specimen morphology. High CR's in combination with corrosion product-free surfaces is an indication that the additive removes corrosion products. When carbon steel corrosion occurs at pH 3 (control), CR is $17.31 \mu\text{m}/\text{y}$ (see surface 1, Figure 3).

In the presence of equimolar concentrations of Ca^{2+} or Sr^{2+} and EDTMP, the corrosion rates are substantially higher, $50.60 \mu\text{m}/\text{year}$ (for Ca^{2+} , surface 2) and $60.38 \mu\text{m}/\text{year}$ (for Sr^{2+} , surface 3). Visual examination of specimens 2 and 3 (Figure 3) reveals that enhanced corrosion is accompanied by surface cleaning by Fe-oxide dissolution. When EDTMP (no metals, at pH 3) is used, CR is $59.89 \mu\text{m}/\text{year}$ and the morphology of the steel surface resembles

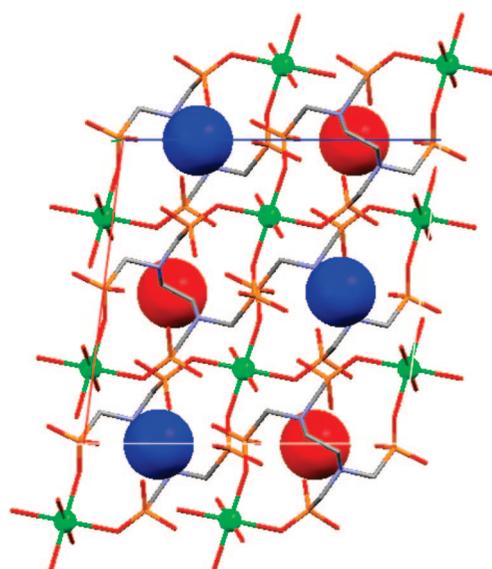


Figure 2. View of water molecules of crystallization, represented as “exaggerated” colored spheres. Blue, above; and red, below the $-\text{CH}_2\text{CH}_2-$ linker.

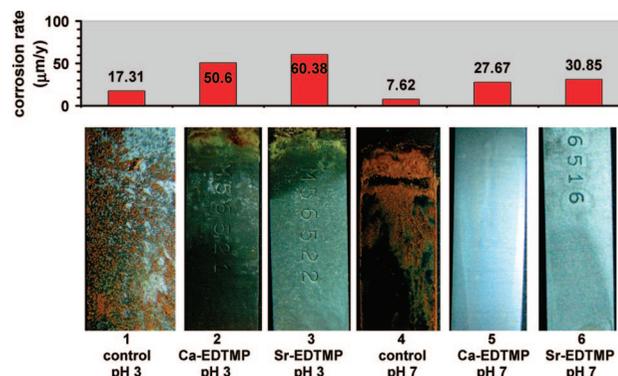


Figure 3. Micromorphology of steel specimens kept at pH 3 and 7. The effectiveness of Ca-EDTMP and Sr-EDTMP as Fe-oxide removers is profound at pH 3 and 7. Corrosion rates higher than the control indicate metal dissolution. Corrosion rate is calculated from the equation $\text{CR} = [534.57 \times (\text{mass loss})]/[(\text{area})(\text{time})(\text{metal density})]$. Units: CR in mm/year , mass loss in mg, area in cm^2 , time in hours, metal density = $7.85 \text{ g}/\text{cm}^3$.

specimens 2 or 3. When the same experiments are repeated at pH 7, CR for the control is $7.62 \mu\text{m}/\text{year}$ (surface 4),¹⁴ whereas it is $27.67 \mu\text{m}/\text{year}$ for Ca^{2+} (surface 5) and $30.85 \mu\text{m}/\text{year}$ for Sr^{2+} (surface 6). As mentioned above, increased CR's indicate that metal loss occurs; however, examination of the steel specimens demonstrates a dramatic chemical cleaning effect. Figure 3 shows that specimens 5 and 6 are free of corrosion products at pH 7. A similar Fe-oxide removal action has been observed when PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid) is used in combination with Ca^{2+} or Zn^{2+} ions.¹⁵ Undoubtedly, high Fe-oxide removal performance is due to the presence of phosphonate moieties with high affinity for Fe^{3+} .¹⁶

To determine the fate of the dissolved Fe^{3+} from the steel specimens, we isolated and studied the byproducts of the Fe-oxide dissolution process. It was demonstrated by FT-IR spectroscopy and elemental analyses that the dissolution product at pH 3 is a Fe-EDTMP complex, if either EDTMP or Ca-EDTMP (1) are used. We synthesized and characterized a Fe-EDTMP compound at pH 3 with a formula $\text{Fe}(\text{EDTMP}) \cdot \text{H}_2\text{O}$, whose FT-IR spectrum matches exactly that of the dissolution product (see the Supporting Information). The dissolution product does not contain any Ca or Sr, but

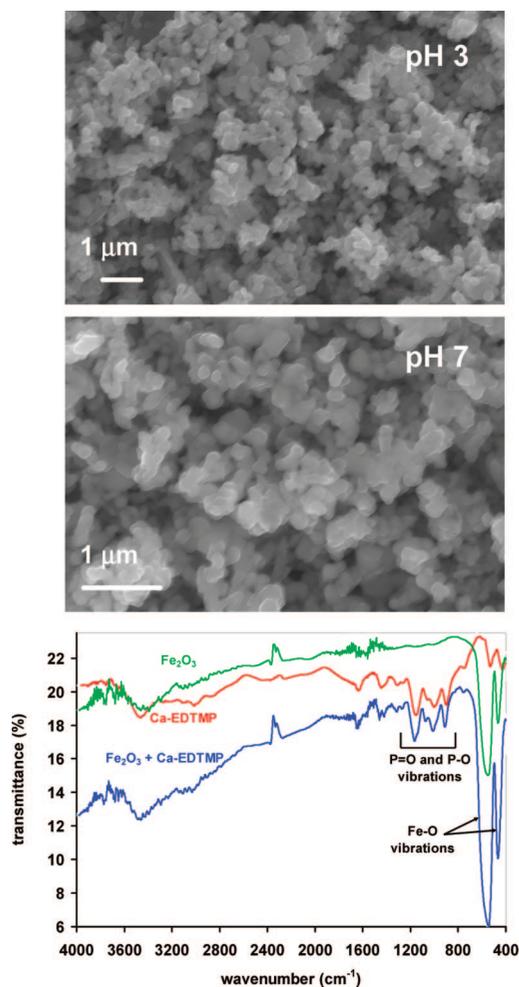


Figure 4. Fe_2O_3 particles isolated after reaction with $\text{Ca}[(\text{EDTMP})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**), upper (pH 3) and middle (pH 7). Ca and P were identified by EDS on the surface of the particles. Comparative FT-IR of Fe_2O_3 , $\text{Ca}[(\text{EDTMP})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**), and of the product of their interaction.

Fe, P, and O were identified (by EDS); therefore, it is likely that $\text{Ca}^{2+}/\text{Fe}^{3+}$ ion exchange has taken place. This is not unexpected, based on the significant differences in stability constants of Fe-EDTMP (20.07^{7a}), Ca-EDTMP (9.29^{7a}) and Sr-EDTMP (7.56^{7b}) complexes. Such $\text{Fe}^{3+}/\text{M}^{2+}$ cation exchange has been observed in similar corrosion protection systems with alkaline earth metal hydroxyphosphonoacetate complexes.^{14b} When the dissolution experiment is performed at pH 7 in the presence of EDTMP alone, only Fe, P and O are identified by EDS. If dissolution takes place at pH 7 in the presence of Ca-EDTMP, the presence of Ca, P, Fe, and O is confirmed by EDS. This is proof that there is an initial interaction of Ca-EDTMP with the Fe-oxide surface. Precipitates were isolated and studied by SEM. Images are shown in Figure 4. Experiments were also carried out that involved reaction of $\text{Ca}[(\text{EDTMP})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) with soluble iron (from $(\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O})$) at pH 3 and 7. Nonstoichiometric and amorphous (by XRD) products were isolated and studied by SEM/EDS and revealed presence of Ca, P, O, and Fe. It is very likely that the noncoordinated P–O moieties complex Fe^{3+} and incorporate it into Ca-EDTMP.

Herein, we described the syntheses and structural characterization of two novel isostructural Ca(Sr)-EDTMP 1D coordination polymers. They contain zwitter-ionic EDTMP²⁻ in an unprecedented chelating/bridging coordination mode. On the basis of our results, use of Ca(Sr)-EDTMP additives for Fe-oxide removal is recommended for pH 7 because they exhibit excellent Fe-oxide dissolution

efficiencies and, at the same time, induce ~50% lower corrosion rates compared to pH 3.

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Supporting Information Available: Crystallographic data (cif files) for compounds $(\text{NH}_4)_2(\text{EDTMP})$, $\text{Ca}[(\text{EDTMP})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**), and $\text{Sr}[(\text{EDTMP})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**2**); elemental analyses, FT-IR spectra, XRD powder patterns, TGA traces, and SEM images (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) **(NH₄)₂(EDTMP)**: EDTMP acid (from Solutia Inc., 1.5 mmol, 0.71 gr) was suspended in ~40 mL of DI water. Using a 1 M NH₄OH stock solution, the pH was adjusted to ~4 and the solid dissolved. This clear colorless solution was left to stand for 1 week. Single

- crystals of $(\text{NH}_4)_2(\text{EDTMP})$ appeared and were isolated by filtration. Yield: 65%. **M-EDTMP** ($\text{M} = \text{Ca}$, **1**; Sr , **2**): EDTMP acid (1.5 mmol, 0.71 gr) was suspended in ~40 mL of DI water. Using a 1 M NH_4OH stock solution the pH was adjusted to ~4 and the solid dissolved. To that clear and colorless solution was gradually added a quantity of the hydrated metal chloride (1.5 mmol, 0.4 gr, molar ratio 1:1) as a solid under constant stirring. The pH dropped, but was readjusted with a 1 M stock solution of NH_4OH to ~4. The homogeneous solution was left at quiescent conditions. After several days single crystals of M-EDTMP ($\text{M} = \text{Ca}^{2+}$, Sr^{2+}) appeared. Crystal growth was allowed to proceed for 2 weeks. The product was collected by filtration and dried in air. Yields: 50% for Ca-EDTMP, 60% for Sr-EDTMP. Further information on full characterization of these products is provided in the Supporting Information.
- (9) X-ray diffraction data were collected on a SMART 1K CCD diffractometer at 298(2) K with $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$). Crystallographic details. **$(\text{NH}_4)_2(\text{EDTMP})$** : rectangular plates ($0.25 \times 0.18 \times 0.08 \text{ mm}$), monoclinic, space group $P2_1/c$, with $a = 8.0117(17) \text{ \AA}$, $b = 6.8313(9) \text{ \AA}$, $c = 16.5259(17) \text{ \AA}$, $\beta = 98.758(11)^\circ$, $V = 893.9(2) \text{ \AA}^3$, and $Z = 2$, $d_{\text{calcd}} (\text{g/cm}^3) = 1.747$, total reflections 5524, refined reflections ($I_{\text{net}} > 2\sigma I_{\text{net}}$) 1794, number of parameters 138, $R_1 = 0.0341$ (0.0385, all data), $wR_2 = 0.0935$ (0.0961, all data), GOF = 1.146. **Ca-EDTMP (1)**: rectangular plates ($0.11 \times 0.08 \times 0.05 \text{ mm}$), monoclinic, space group $C2/c$, with $a = 13.206(3) \text{ \AA}$, $b = 10.368(2) \text{ \AA}$, $c = 13.763(3) \text{ \AA}$, $\beta = 97.367(18)^\circ$, $V = 1868.9(7) \text{ \AA}^3$, and $Z = 4$, $d_{\text{calcd}} (\text{g/cm}^3) = 1.877$, total reflections 5926, refined reflections ($I_{\text{net}} > 2\sigma I_{\text{net}}$) 1766, number of parameters 147, $R_1 = 0.0362$ (0.0439, all data), $wR_2 = 0.1052$ (0.1094, all data), GOF = 1.077. **Sr-EDTMP (2)**: blocks ($0.25 \times 0.18 \times 0.13 \text{ mm}$). Crystals are monoclinic, space group $C2/c$, with $a = 13.449(4) \text{ \AA}$, $b = 10.3649(18) \text{ \AA}$, $c = 13.912(5) \text{ \AA}$, $\beta = 98.40(2)^\circ$, $V = 1918.5(9) \text{ \AA}^3$, and $Z = 4$, $d_{\text{calcd}} (\text{g/cm}^3) 2.000$, total reflections 5969, refined reflections ($I_{\text{net}} > 2\sigma I_{\text{net}}$) 1898, number of parameters 141, $R_1 = 0.0256$ (0.0291, all data), $wR_2 = 0.0701$ (0.0717, all data), GOF = 1.040. Copies of crystallographic data for the following structures may be obtained free of charge from the CCDC: $(\text{NH}_4)_2(\text{EDTMP})$, ref. no. 625197; Ca-EDTMP (**1**), ref. no. 605561; Sr-EDTMP (**1**), ref. no. 603911.
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- (13) **Carbon steel surface cleaning protocol**. A modified protocol was based on NACE Standard TM0169–95 (item 21200), National Association of Corrosion Engineers, Houston TX. Corrosion specimens (carbon steel C1010) are prepared according to the above protocol. Each specimen (carbon steel C1010 from Metal Samples Corrosion Monitoring Systems, Munford, AL) is immersed in a control solution (no inhibitor) or in a test solution (10.0 mM M^{2+} and 10.0 mM EDTMP at pH 3 or 7) and corrosion progress is monitored by visual inspection for ~6 days. Then the specimens are removed from solution, surface samples are taken for spectroscopic studies and corrosion products are cleaned by the standard method above to determine corrosion rates from mass loss based on the above NACE Standard.
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