

Study Cum Research on Effect of Addition of Organic and Inorganic Acids in Naturally Bonding Sand Used in Metal Casting

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Abstract

We have investigated the effect of addition of some of the inorganic and organic acids, in the naturally bonding sands taken from the bank of river Ravi, Lahore, Pakistan, on quality of casting and on mechanism of their reinforcement in the moulding sand. The test bars are cast in the moulding sands after adding little quantity (2%) of the following acids: H_3PO_4 , Tartaric acid ($C_4H_6O_6$), Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) and HCl. It has been found that phosphoric acid H_3PO_4 is the only acid which increases the mechanical resistance of the moulding sand in which it has been added and fulfills the requirements of greensand moulds which can be used for metal casting. The anions produced by the dissociation of phosphoric acid change the ions of 'first diffused layer' of clay to the normal ions of Mg^{++} , Ca^{++} , K^+ , Na^+ and hydrogen. Retaining samples in the air for 20-30 min. largely improves dry compression strength, dry shear strength and resistance to torsion of the samples (see text). Studies with Scanning Electron Microscope have revealed that phosphoric acid dissociates into hydrogen and $H_2PO_4^-$ which develops cementitious compounds on self hardening. On the temp of the sand mould the conjugate $H_2PO_4^-$ further dissociates and phosphorous having high affinity for O_2 , oxidizes into the free oxides (see SEM images). Oxalic acid has the great capacity to leach iron oxide present in the clay at pH value 2.5-3 and temp. above $90^\circ C$. Tartaric acid do not have any significant effect because its conjugates do not impart any mechanical resistance to the moulding sand. HCl dissociates and Cl liberated enters in the Skelton of the clay and reduces its mechanical strength. However author recommends that work on these acids addition in moulding sand, particularly the leaching effect of oxalic acid on the oxides of iron, present in the clays and silica sands, may be carried out further.

Keywords: H_3PO_4 , $C_4H_6O_6$, $H_2C_2O_4 \cdot 2H_2O$ and HCl, addition in moulding sand, Effect on mechanical resistance, SEM images of sand samples.

Introduction

Moulding sands are mixtures of three or more ingredients. A green sand contains clay and water, as well as the principal sand constituent, SiO_2 . These three components provide the bulk and plasticity required by the moulding sand. Other materials may be added to the sand mixture to enhance certain properties.

Clay does not fulfill optimum conditions of good mechanical strength needed for casting in green sand mould made by its addition. Therefore it is pulverized mechanically or it is chemically treated to increase its binding strength. Fine ground natural clay increases compression strength of moulding material about 30% [9]. However it has been observed that little quantity of bentonite added in moulding material exhibit almost same results [10].

Casting experiments

We have investigated the effect of addition of some of the norganic and organic acids, in the naturally bonding sands taken from the bank of river Ravi, Lahore, Pakistan, on quality of casting. The test bars (fig.1) are cast in the moulding sands after adding little quantity (2%) of the following acids:

1. Phosphoric acid (H_3PO_4)
2. Tartaric acid ($C_4H_6O_6$)
3. Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) and

4. Hydrochloric acid (HCl)

Nomenclature and some of the important properties of these acids are given in table 1 & fig. 1.

Sands from sedimentary deposits occurring on banks or in pits of rivers and lakes usually contain less than 5 per cent clay and can be used for making moulding sands and core sands for utilizing for metal casting. Upper layer of the sand of the river bank is coarse and is used for construction purposes while lower layer is composed of fine grains which are used in foundries. Additional 5% bentonite is added for developing plasticity, mouldability and good mechanical resistance.

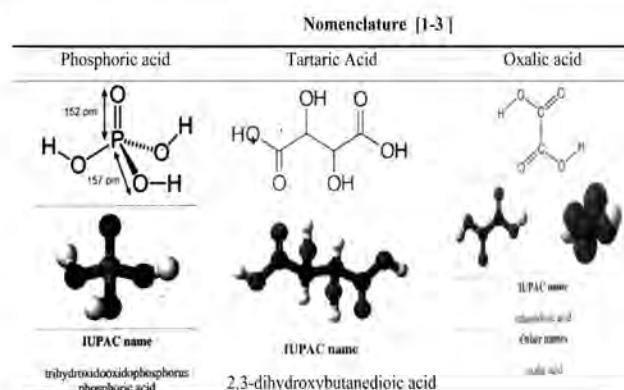


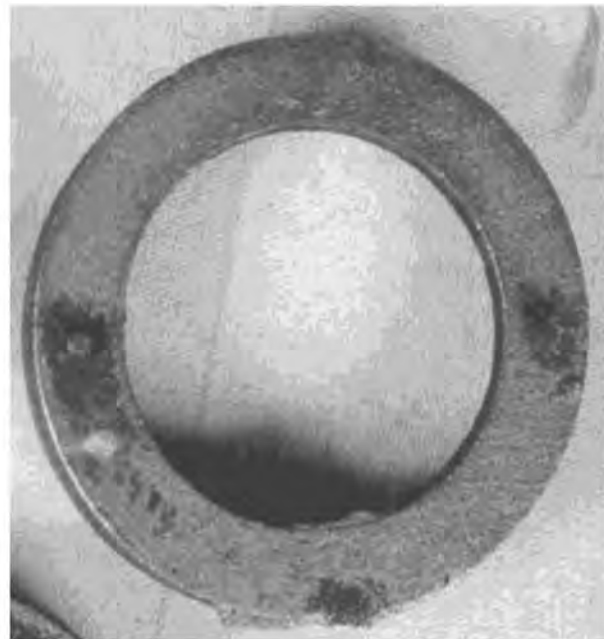
Fig. 1 Nomenclature of Acids

Table 1. Physical properties of the acids used [1-4]

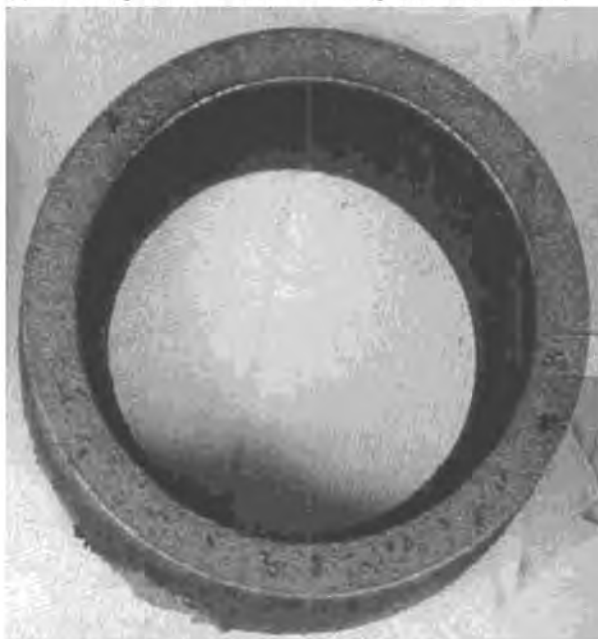
Properties	Phosphoric acid	Tartaric Acid	Oxalic acid
Molar mass	98.00 g/mol	150.087 g/mol	90.03 g/mol ⁻¹
Appearance	White solid or colourless viscous liquid	White powder	White crystals
Density	1.885 g/mL (liquid) 1.685 g/mL (85% solution)	1.79g/mL	1.90 g/cm ⁻³
Melting point	42.35 °C (anhydrous) 29.32 °C *hemihydrates)	171-174°C (L-tartaric) 206°C (DL,146-148°C(meso)	189-191°C, 462-464K, 372-376 °F
Solubility in water	5.48 g/mL	133g/100ml(20°C)	90 g dm ⁻³ (at 20°C)



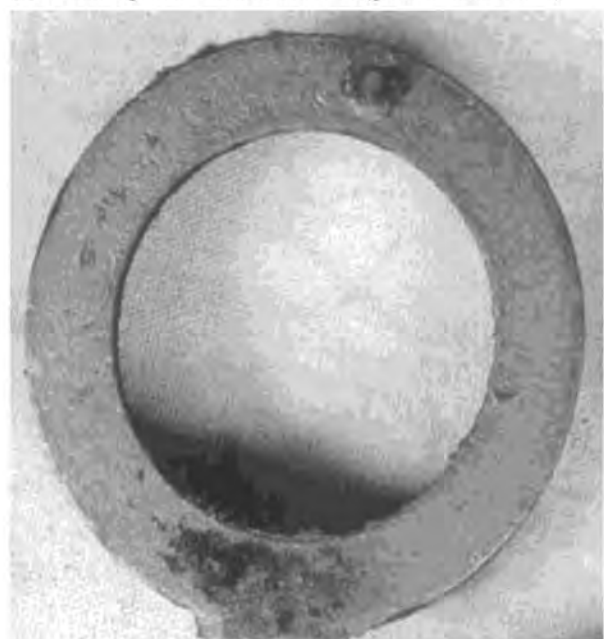
(a) Moulding sand + tartaric acid 2% (good surface finish)



(b) Moulding sand + oxalic acid 2% (good surface finish)



(c) Moulding sand + phosphoric acid 2% (bright & good surface finish)



(d) Moulding sand + hydrochloric acid 2% (bright & good surface finish)

Fig. 2 Effect of acid additions in naturally bonding sands, on the surface finish of test bar castings*

* discarded immediately after solidification. Presented without fettling

2. Results

2.1 Mechanical properties

Table 2. Mechanical resistance of moulding sand* after addition of acids

Mech. Property	H ₃ PO ₄ 2%	HCl 2%	Tartaric acid 2%	Oxalic acid 2%	Min. limiting value for a good green sand mould used in foundry practices:
Green compression strength	3.5 N/cm ²	2.5 N/cm ²	2.4 N/cm ²	1.8 N/cm ²	Obs No. 1
Green Shear strength	4.5 N/cm ²	3.5 N/cm ²	2.5 N/cm ²	2.0 N/cm ²	
Permeability	125	107	115	120	125-130

* Composition: Naturally bonding sand + 5% bentonite + 5% water

** Obs.1 2-3.5N/cm² after Titov, N.D and Y.U Stephnov, 1982

Table 3. Mechanical resistance of moulding sands blended with 1.5% H₃PO₄ after drying [7] [11]

Dry compression St.	Dry shear St.	Dry torsion St.	Comments
87.5 N/cm ²	87.5 N/cm ²	30 N/cm ²	On drying the samples are self hardened

2.2 Moulding properties

Table 4. Moulding properties of the moulding sands after addition of acids as noted during moulding

Moulding Property	H ₃ PO ₄ 2%	HCl 2%	Tartaric acid 2%	Oxalic acid 2%	Comments
Green compression strength	Good	Inferior	Inferior	Poor	Green sand blended with phosphoric acid is somewhat suitable for foundry practices
Green Shear strength	Good	Inferior	Inferior	Poor	-do-
Dry compression strength	Excellent	Inferior	Poor	Poor	Mould blended with phosphoric acid had shown high dry strength. see also ref. [11]
Permeability	Good	Low	Low	Good	Green sand blended with phosphoric acid and HCl have proper permeability as required for greensand moulds
Flowability	Good	Good	Good	Good	All sands blended with acids showed good flowability
Compactability	Good	Good	Good	Good	Show good compactability after ramming
Edge hardness	Sufficient	Sufficient	Sufficient	Sufficient	Greensand moulds made with addition different acids have adequate edge hardness. They produce sound castings without defect "crush"

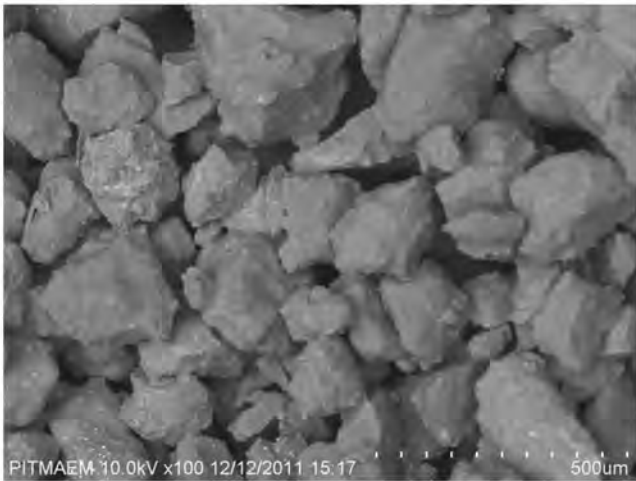
2.3 Casting quality

Table 5. Quality of test bars of iron castings made in sand moulds blended with acids (Ref. fig. 1)

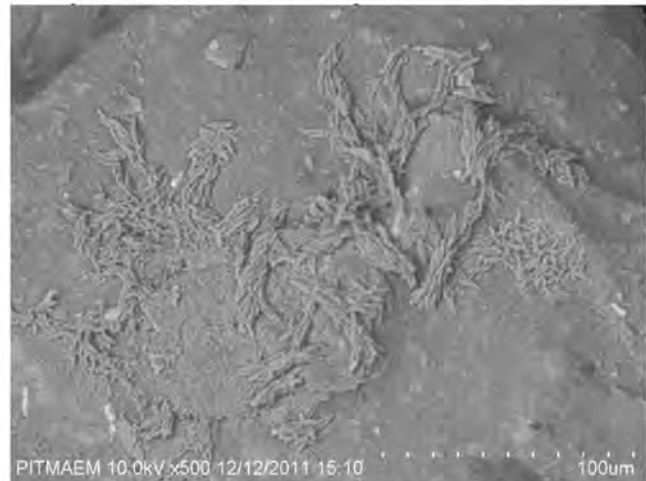
Casting quality	H ₃ PO ₄ 2%	HCl 2%	Tartaric acid 2%	Oxalic acid 2%	Comments
Defect analysis					Maintaining proper ingredients in the moulding sand, produced defect free castings. Acid additions do not have shown adverse effect, as far as, appearance of casting defects, is concerned.
Sand bun on	Nil	Nil	Nil	Nil	
Blowholes	-do-	-do-	-do-	-do-	
Hot & cold tears	-do-	-do-	-do-	-do-	
Macro and micro Shrinkage	-do-	-do-	-do-	-do-	
Surface finish	125µm	125µm	125µm	125µm	See Observation No. 1
Surface quality	Bright	Bright	Dull	Dull	See Observation No. 2

Observation 1: (1) Good surface quality = 90µm (2) general rigosity of castings made in sand moulds >100 (3) precise finishing 0.2µm (4) good surface finish = 1.6 µm (5) economical finishing = 6.3µm (7) rough finishing = 25µm (courtesy PITAC, Lahore)

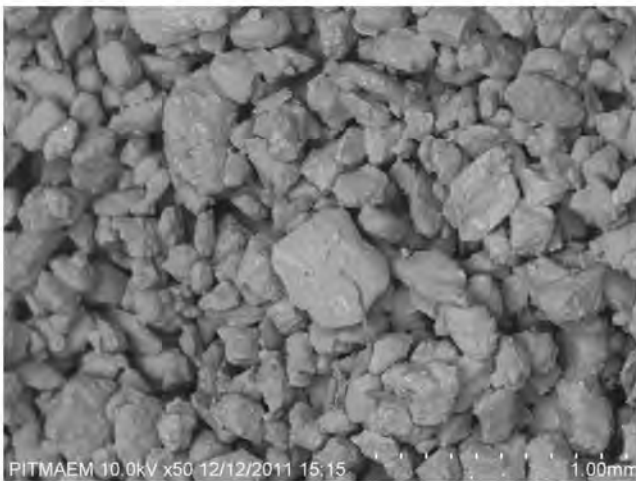
Observation 2: Inorganic acids leaches the sand thus their surfaces are comparatively brighter.



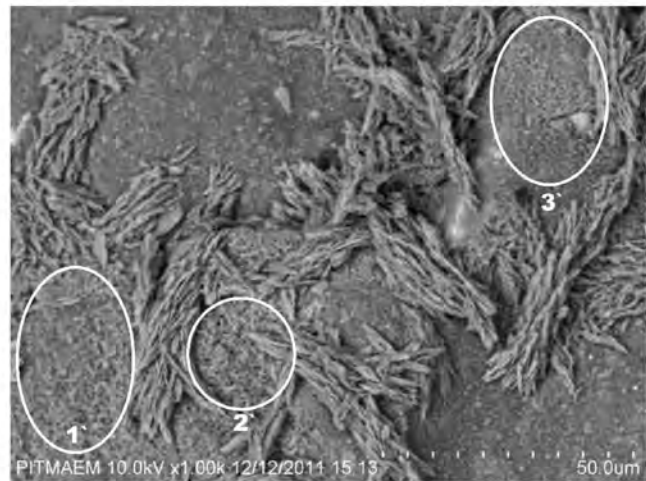
(a) Moulding sand + 2% phosphoric acid (SEM image at low Mag 50x) particles of sand are visible



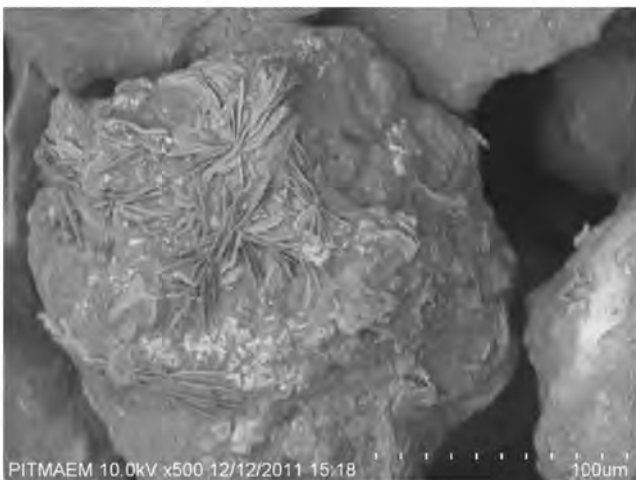
(d) Moulding sand + 2% phosphoric acid (An other SEM image at Mag 500x). Deposition of phosphoric acid on the sand grains in an irregular way



(b) Moulding sand + 2% phosphoric acid (SEM image at Mag 100x) particles of sand are visible. However the traces of phosphoric acid are still not visible at Mag. 100

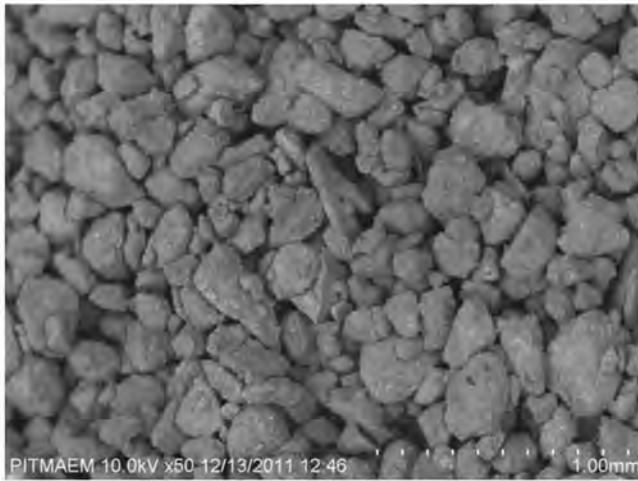


(e) Moulding sand + 2% phosphoric acid (SEM image at Mag 1000x). Image showing the deposition of phosphoric acid on the sand grains at larger magnification dissociation products and cementitious compounds (1,2,3)

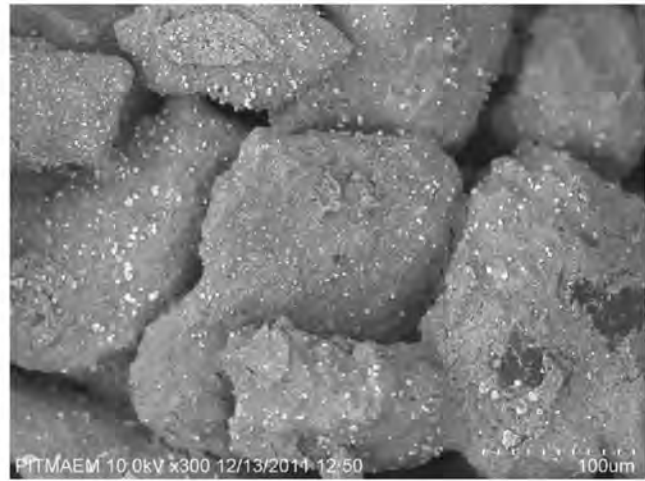


(c) Moulding sand + 2% phosphoric acid (SEM image at Mag 500x). Phosphoric acid is dissociated and deposited on the surface of sand grains in the form of rosette

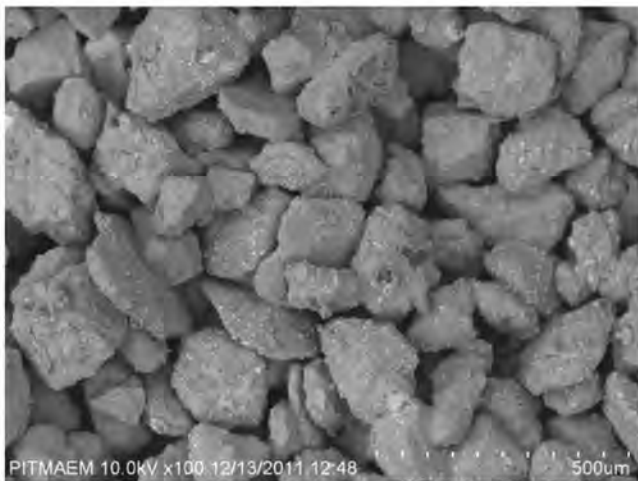
Fig. 3 Scanning Electron Microscope (SEM) Images of moulding sand blended with phosphoric acid



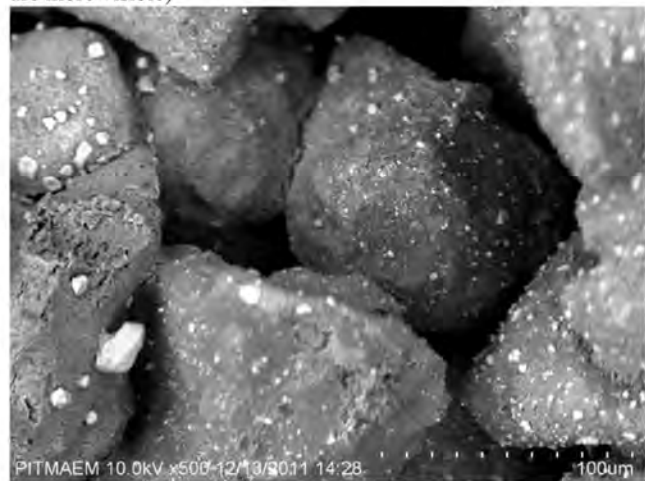
(a) Sand sample taken after casting (SEM image at low mag. x50 grains are visible)



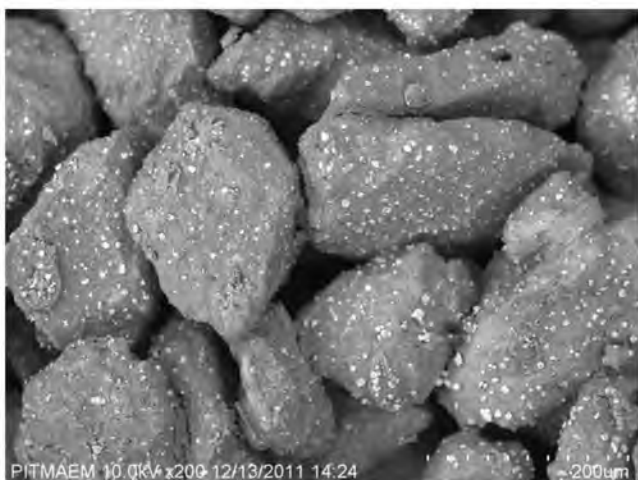
(d) Sand sample taken after casting (SEM image at mag. x300 particles of phosphoric acid, after dissociation sticking with grains are more visible)



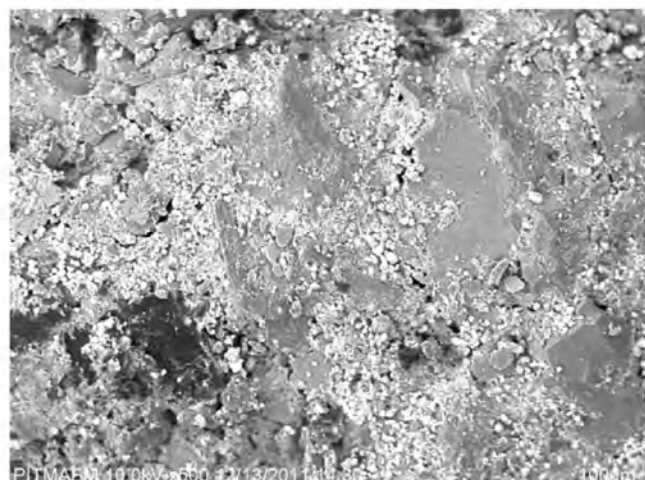
(b) Sand sample taken after casting (SEM image at mag. x100 particles of phosphoric acid sticking with grains)



(e) Sand sample taken after casting (SEM image at mag. x500 particles of phosphoric acid which have not dissociated are sticking with grains, are more visible)



(c) Sand sample taken after casting (SEM image at mag. x200 particles of phosphoric acid, after dissociation sticking with grains are more visible)



(f) Sand sample taken after casting (SEM image at mag. x500 particles of conjugates of phosphoric acid, who have oxidized intensely by the heat dissipated by the casting to the mould wall)



(g) Sand sample taken after casting (SEM image at mag. x1000 particles of phosphoric acid sticking with grains, and cementitious compounds (1,2)



(h) Sand sample taken after casting (SEM image at mag. x1000) particles of phosphoric acid and cementitious compounds (1-6)

Fig. 4 Scanning Electron Microscope (SEM) Images of moulding sand blended with phosphoric acid. (Sand sample taken after complete solidification of casting)

Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) Images of moulding sand blended with phosphoric acid*

- Moulding sand + 2% phosphoric acid (SEM image at low Mag 50x) particles of sand are visible
- Moulding sand + 2% phosphoric acid (SEM image at Mag 100x) particles of sand are visible. However the traces of phosphoric acid are still not visible at Mag. 100
- Moulding sand + 2% phosphoric acid (SEM image at Mag 500x). Phosphoric acid is dissociated and its conjugates ($H_2PO_4^-$) deposited on the surface of sand grains in the form of rosette.
- Moulding sand + 2% phosphoric acid (An other SEM image at Mag 500x). Deposition of phosphoric acid on the sand grains in an irregular way
- Moulding sand + 2% phosphoric acid (SEM image at Mag 1000x). Image showing the deposition of phosphoric acid on the sand grains at larger magnification (dissociated projects and cementitious compounds, 1,2,3)

* by courtesy of PITMAEM (SEM section), Pakistan Council of Scientific and Industrial Research, Lahore complex, Pakistan/

Discussion on Physico Chemical processes which take place at the active surface of the sand mould blended with acids [1-4] [6-11] [13-22] [25-35].

Bonding film formed by clay

Moist clay is the bond or binder of moulding sand. The bonding forces involved in holding particles of clay together may be accounted for by several theories: electrostatic bonding, surface tension forces, and interparticle friction bond. The mechanism of electrostatic

bonding of clays may be described as a network of dipolar forces operating at the sand-clay and clay-clay interfaces. This network of forces is initiated by the preferential adsorption of positive ions and negative ions on combined water and clay (hydrated) surfaces. Fig. 5 shows a micelle or hydrated clay particle.

Why water is added to a dry clay, the negative ions are adsorbed on the nuclei of the clay atoms and form an integral part of the crystal. The positive ions are attracted by the negative ions, but repelled by the nuclei of the clay atoms, with the result that the positive ions take up equilibrium positions. The water forms neutralized clay micelles whose kinetic energy causes them to move toward on another. There is thus then a force of attraction between positive ions themselves and the nuclei of the clay particles (see Fig. 6). As the distance between the clay micelles increases, the force of attraction increases and that of repulsion decreases, resulting in a net intermicellar force.

The drawing together of two micelles causes the orientation of unlike ions, forming a clay dipole (fig. 7), and a maximum attractive force is at an optimum distance of separation x . There are many such dipoles in a clay-water medium. Depending on the type of clay, a maximum degree of hydration is necessary to develop a dipole completely. This is why the strengths of clay-bonded sands increase with increasing amounts of water, up to a maximum value. As the amount of water is increased further, water enters the spaces between the dipoles to a distance greater than x (fig. 8), resulting in a decrease in the net intermicellar force.

Surface tension of the water surrounding the clay and clay-sand particles provides another possible source of bond strength. The interstices of the clay particles are filled with water. The surface layers of water act on a stretched membrane of hydrated clay, forcing the clay particles together. When the amount of water is reduced by drying, the force holding the particles together increases.

The geometry of the aggregate can provide another force adding to the strength of the bond between particles.

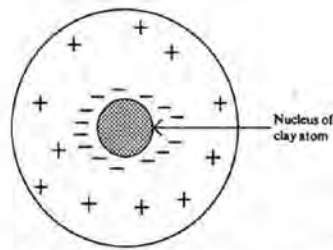


Fig. 5 A clay dipole. Surrounding the particle of clay are negatively charged hydroxyl ions positioned at varying distances from the particle. Outside this layer are positively charged ions (usually hydrogen ions) also located at varying distances from the particle; hence the term *double diffuse layer*. This layer is rigidly attached to the surface of the particle and is considered to behave as a solid. (Courtesy American Foundrymen's Society.)

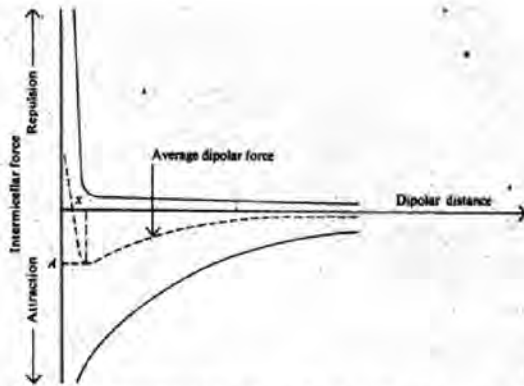


Fig. 6 The forces of attraction and repulsion as a function of dipolar distance. The critical spacing is defined as x units and the maximum bond is A . (Courtesy American Foundrymen's Society.)

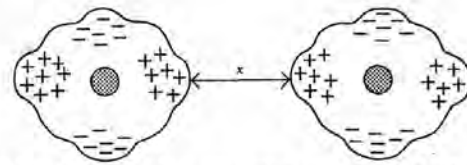


Fig. 7 Micellar dipoles, indicating the localized concentration of adsorbed negatively charged hydroxyl ions (-) and positively charged ions (+); x denotes critical intermicellar spacings, the result of a compromise between the forces of attraction and repulsion.

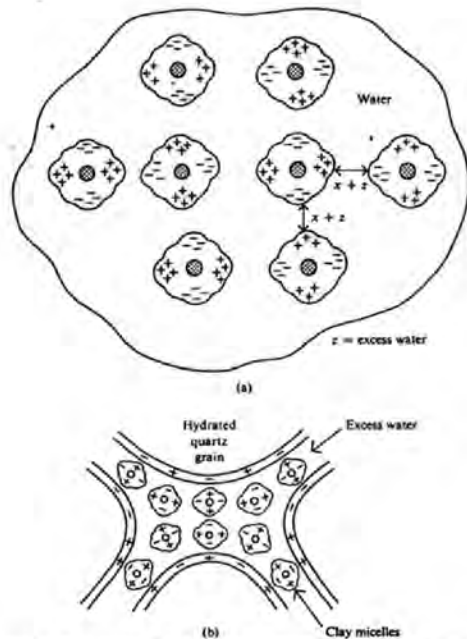


Fig. 8 (a) Dipole alignment of hydrated clay particles (condition of minimum free energy) in a water medium (green state). (b) Schematic sketch showing disposition of clay and quartz dipoles. In green sand the intermicellar voids are filled with water. (Courtesy American Foundrymen's Society.)

The theory of interparticle friction, or the so-called block-and-wedge theory, involves materials under pressure. When molding sand is rammed inside a flask, the particles are jammed against their neighbors. Sand which is rammed to a certain shape and which resists deformation is held together through interparticle friction.

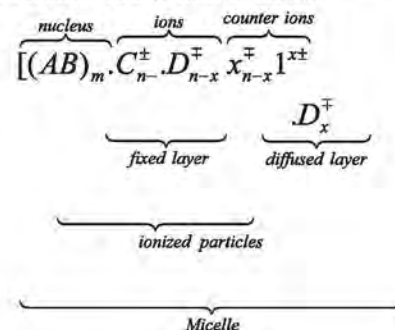
A positive relationship was obtained between pH and the percentage of dispersible clay for each soil clay. The percentage increase in net negative charge was also positively correlated with pH. In general, the net negative charge was the primary factor in clay dispersion and the pH affected clay dispersion by changing the net charge on clay particles [21].

Binding film formed by bentonite

Particles of montmorillonite are constituted in rows of fragmented channels. Due to fragmentation, on the corners and peaks and on the surfaces, which are exposed, a number of anions with free valences are produced and due to this, these particles bear the negative potential. Together particle of montmorillonite, it may be termed as 'macro anion'. When particles of the montmorillonite come in contact with water (electrolyte), it develops adsorption of cations on the surface of macro anions. The cations

adsorbed from the liquid will form an ionic pool or '1st diffused layer' as shown in the fig. 9.

Cations adsorbed form ionic bond which have a tendency of hydration and attract the molecules of polarized water (dipoles). In this way, '1st diffused layer' is formed in between water layer and particle of bentonite, which envelops the particles of montmorillonite. The thickness of the layer is 3.10^{-5} cm [11]. Molecules of water from this layer are retained by great force, due to this reason, the water from this layer is very viscous. Structure formed by ions and cations is called 'micelle'. The transportation of ions and cations formed by the first and second layer diffused is shown as follows:



In this context schematic representation of bonding in some of the moulding materials are given in fig. 10(a-e). Fig 10(a) represents dry moulding material while fig. 10(b) represents the same moulding material but little damped without any bonding material. The fig.10(c) represents the layer of water linked firmly with micelle of quartz. Fig. 10(d) represents moulding material made with the water and inorganic binding material while structure of micelle is shown in fig. 10(e).

Mechanism of film formation and bond, in moulding material, based on sand and bentonite, is illustrated in fig11. From fig 10 and 11, it can be observed that in presence of water, sand and bonding material, some 'pseudo colloids' are developed, forming 'micelle' During mixing and ramming, 'intermediate layer of rigid water' enters in reactions with micelle creating a strong bond between the grains of the moulding mixture.

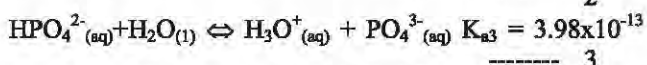
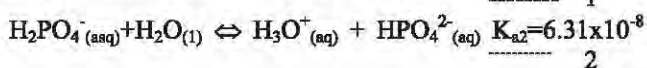
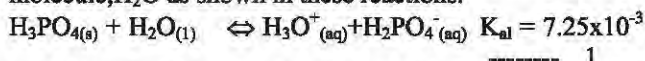
Pseudo colloidal solutions, which are formed in moulding materials made from bentonite are characterized by high viscosity therefore assure the mechanical strength of the sand mould in green state. During process of mixing, forces between diversified grains and intergranular friction weaken the bond of binding material. These phenomena bring about increase in number of free valences and decrease in mechanical resistance of moulding material. Bentonite with high content of montmorillonite envelops the sand grains with continuous film of bonding material as illustrated in fig. 12(a).

In case of clay continuous film is not formed, while it agglomerates on the surface of sand grains as illustrated in fig 12(b). This explains high mechanical strength and high permeability of moulding material made from bentonite as compared to those made by the addition of clay.

Some bentonites develop high acidity. The Hancili bentonite from Turkey shows significant changes in surface area, micro and mesoporosity, surface acidity and acid strength with heating from 100 to 900°C for 2 hr. The total surface acidity, in general, declines with increasing temperature. The most acidic sites, however, increase with heating, and especially at dehydration and dehydroxylation. Acid strength reaches its maximum during the dehydroxylation phase at ~600°C. It was concluded that the total surface acidity does not necessarily parallel the strength of the most acid sites [20].

Characterization of acid stabilization Phosphoric acid [2]

Phosphoric acid (which is also called orthophosphoric acid) molecule can dissociate up to three times, giving up an H⁺ each time, which typically combines with a water molecule, H₂O as shown in these reactions.



The anion after the first dissociation, H₂PO₄⁻, is the dihydrogen phosphate anion. The anion after the second

dissociation, HPO₄²⁻ is the hydrogen phosphate anion. The anion after the third dissociation, PO₄³⁻, is the phosphate or orthophosphate anion.

Because the triprotic dissociation of phosphoric acid, its conjugate bases (the phosphates mentioned above) cover a wide pH ranges. It is, therefore, phosphoric acid widely used as hardener in moulding sands and sand made by the addition of phosphoric acid produce cores that can be easily knocked out of the casting.

Author have studied the morphology of cementitious compounds and mechanism of hardening of mould sand on addition of phosphoric acid with the help of electron microscope (SEM). SEM images of moulding sand treated with H₃PO₄, at different magnification, in green state as well as, after complete solidification of casting, are presented in fig. 3 and 4, respectively. Fig. 3 (a&b) show the image of SEM at low magnification, respectively 50x and 100x. At these magnification the particles of sand are visible. These are of irregular shape. However particles of phosphoric acid and its conjugates, products after dissociation are still not visible at this magnification.

Phosphoric acid or its anions of its dissociation (see reaction 1 - 3) stick cementitously with the particles of sand, are shown in fig. 2 (c &d) (they appear in rosette form or have scattered in irregular form) At high magnification cementitious zone are visible (fig. 3 (e) mag. 1000x).

It has already been explained that mech. strength of bentonite is due to first diffused layer (adsorption of cations of water on macro anions of montmorillonite, forming ionic pool) which is further reinforced by second diffusion layer (adsorption of polarized water in ionic pool).

The anions produced by the dissociation of phosphoric acid change the ions of first diffused layer to the normal ions of Mg²⁺, Ca²⁺, K⁺, Na⁺ and hydrogen ions [11]. This is why that green sand moulding material based on chemical treatment show lower degree of mech. resistance (table 2 and when it is dried by self hardening, it shows high dry compression and shear strength (table 3) [9, 11].

Phosphoric acid reacts with free ion and aluminum oxides present in clays, producing heat and rapid formation of insoluble hard cementitious products (winterkorn 1962). According Buzila S, (1976) [9-10] and Habibullah P (2012) [7] compression strength of phosphoric acid treated sample resulted in an almost three fold strength improvement in comparison with that not treated with phosphoric acid. It is, therefore, phosphoric acid widely used as hardener in moulding sands and sand made by the addition of phosphoric acid produce cores that can be easily knocked out of the casting.

Mechanical resistance of moulding material is inversely proportion to the content acid added. Negative effect of addition of acid in greensand mould increases with the time. This is due to the rupture and relaxation in diffused layers of micelles formed on surface of quartz grains by gel of clay water. From this, the conclusion can be drawn that with passage of time the electrostatic charges are neutralized and so the total water present in the layers of clay and sand grains is transformed from rigid water to the free water. The free water appeared in this

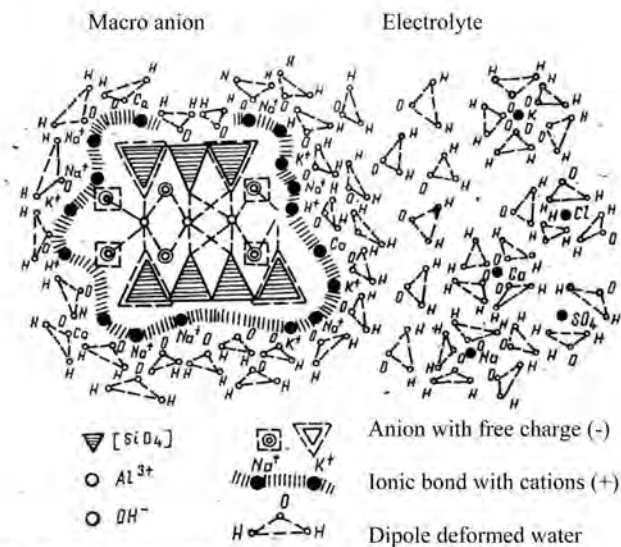


Fig. 9 Ionic bond [Buzila S, 1976] [8]

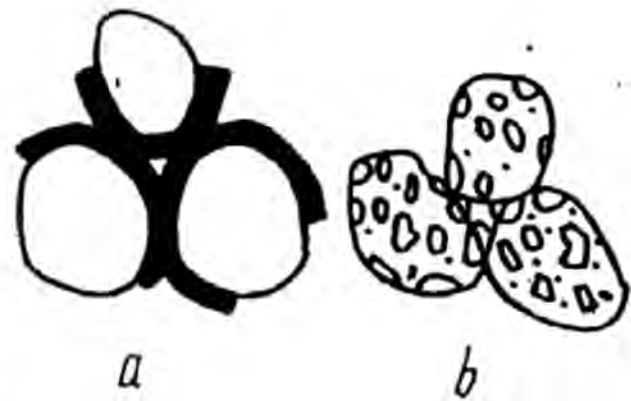


Fig. 12 Repatriation of bentonite (a) and clay (b) on the surface silica grains

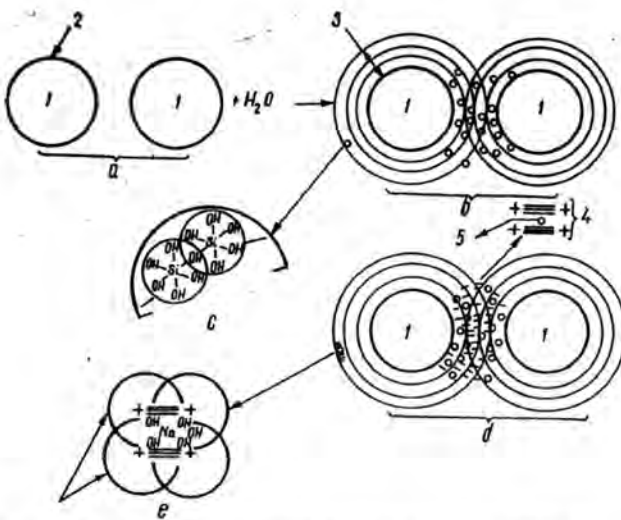


Fig. 10 Some moulding materials having inorganic additives (schematic) [Buzila S, 1976] [8] (1) Nucleus of quartz (2) layer of amorphous SiO₂ (3) water linked with quartz particle (4) montmorillonite particle (5) ion adsorbed

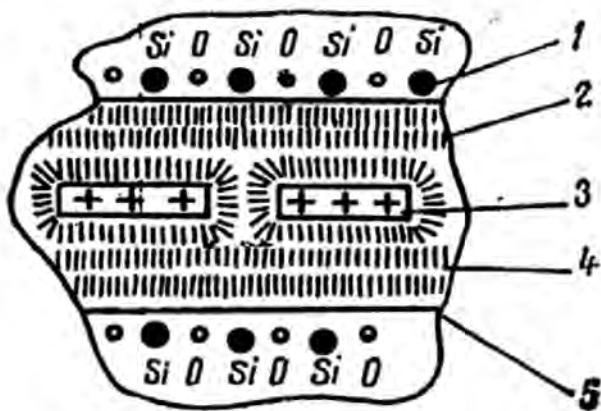
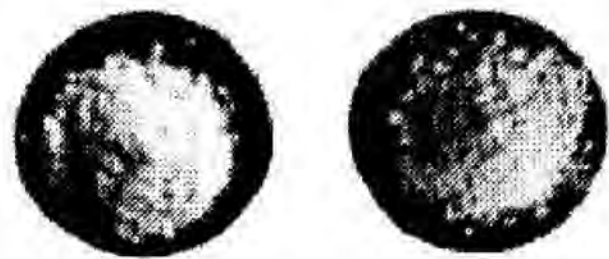


Fig. 11 Mechanism of film formation and bond in moulding material made by addition of bentonite [Buzila S, 1976] [8] (1 & 5) quartz grain (2 & 4) rigid water layer linked with quartz and bonding material (3) bonding material particle



50x

Fig. 13 Photograph of the China clay before (right) and after (left) leaching with the oxalic acid [25]

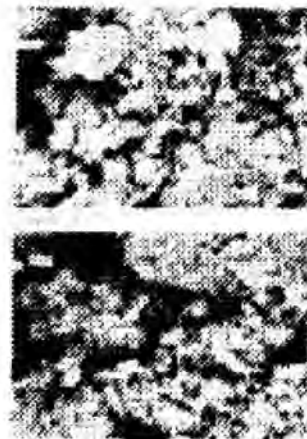


Fig. 14 SEM image of China clay after (upper) and before (lower) treatment with oxalic acid [25]

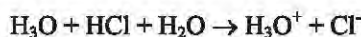
transformation decreases the binding properties of clay and therefore, also, decreases the mechanical resistance of the moulding material. The maximum time of hardening of core in air made by addition of phosphoric acid in core sand is recommended as 10-30 min.

Fig. 4(a-h) show SEM image of the moulding sand samples taken after complete solidification of the casting in the mould. At low magnification 50x and 100x, grains of moulding sand are visible, fig. 4 (a&b). At some higher magnification 200x and 300x particles of phosphoric acid and its anions are visible as sticking on the surface of moulding sand particles, fig.4 (c&d). At 500x mag., the oxides formed after intense oxidation of products of dissociation of phosphoric acid, coated and bound with sand particles are visible fig. 4 (e&f). this illustrates that compounds of phosphoric acid have been vigorously oxidized under effect of heat dissipated by solidifying casting and have transformed the clay into the integrated structure. The chemical reaction has developed cementitious areas which are visible in fig. 4(g&h)

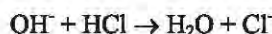
In general, two basic phosphate reactions are distinguished with Al and Fe oxides and hydroxides. The initial reaction appears to be a fast ligand exchange of surface hydroxyl groups with phosphate and the formation of inner-sphere surface complexes (Laiti et al 1996; Nanzyo 1984; Persson et al.1996). On the other hand, for the longer term reactions, two possible mechanisms have been suggested. The first one involves the slow diffusion of phosphate ion into micropores (van Riemsdijk et al.1984). Another proposed mechanisms is the slow weathering of surface in the presence of phosphate and the formation of metal phosphate precipitate (Laiti et al. 1996; Lookman et al. 1997; Li and Stanforth 2000). In the present paper an attempt was made to identify the mechanisms responsible for the improvement of phosphoric acid.

Effect of HCl [4]

Hydrogen chloride (HCl) is a monoprotic acid, which means it can dissociate (i.e., ionize) only once to give up one H⁺ ion (a single portion). In aqueous hydrochloric acid, the H⁺ joins a water molecule to form hydronium ion,



The other ion formed is Cl⁻, the chloride ion. When chloride salts such as NaCl are added to aqueous HCl they have practically no effect on pH, indicating that Cl⁻ is an exceedingly weak conjugate base and that HCl is fully dissociated in aqueous solution. Hydrochloric acid is the monoprotic acid least likely to undergo an interfering oxidation-reaction. Hydrochloric acid can be used to regulate the acidity (pH) of solutions.



High quality hydrochloric acid is used in the regeneration of ion exchange resins. Cation exchange is widely used to remove ions such as Na⁺ and Ca²⁺ from aqueous solutions, producing demineralized water. The acid is used to rinse the cations from the resins.

Na⁺ is replaced by H⁺
Ca²⁺ is replaced by 2H⁺

Clays are not truly soluble in HCl acid, exposure to HCl acid does affect the structure of clay minerals. Only chlorite was found to be the most susceptible to acid attack. The reaction of acid on chlorite was found to be dependent upon HCl strength and temperature. Diffraction studies, coupled with fluid analyses, revealed that the mechanisms of acid attack is the leaching of ions from the matrix of chlorite clay.

The addition of HCl in the sand moulds decreases its compression and shear strength. On drying, the phosphoric acid acts reversely to the HCl, in former case mechanical strength increases 3.0 to 3.5 times, while in later case it comes to half times. This can be explained, in this way that in water solution, HCl dissociates totally in hydrogen and chlorine ions. While phosphoric acid dissociates in hydrogen ions and radical H₂PO₄⁻. On drying, the chlorine ions enter in the spatial Skelton of clay, destroy it, while radical H₂PO₄⁻ forms a spatial Skelton of higher mechanical resistance [Buzila S.1976].

Effect of Tartaric acid [3]

Tartaric acid is a white crystalline diprotic organic acid and is commonly combined with baking soda to function as a leaving agent in recipes, and is one of the main acids found in wine. It is added to give a sour taste, and is used as an antioxidant.

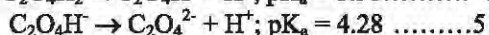
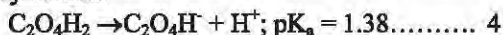
Melting point of tartaric acid is: 171-174°C (L-tartaric), 206°C (DL, racemic), 146-148°C (meso). At mould temp. it dissociates. The casting experiments conducted to judge the effect of tartaric acid on strength of the mould used for metal casting have shown that it lowers the mech. resistance of the samples and green compression strength and green shear strength were much less than the moulding sand treated with phosphoric acid (table 2). It is due to the fact that tartaric acid could not fix the pH value of the liq. components in moulding sand and does not produce any stable compound on dissociation. Its K, Na, Sb derivatives do not have any cementitious characteristics. They are in the form of cream. Its aqueous solution can only dissolve Cu (II) oxide layer. Tartaric acid is muscle toxin therefore it should be used carefully.

Effect of oxalic acid

Oxalic acid is an organic compound with the formula H₂C₂O₄. Oxalic acid is a reducing agent and its conjugate base, known as oxalate (C₂O₄²⁻) is a chelating agent (one ion connected with two bonds in a ring structure) for metal cations. Typically oxalic acid occurs as the dehydrate with the formula H₂C₂O₄. 2H₂O. Melting point of oxalic acid is 189-191°C (see table 1). At temp. of sand mould during solidification of casting, the oxalic acid dissociates.

Anhydrous oxalic acid exists as two polymorphs; in one the hydrogen-bonding results in a chain-like structure whereas the hydrogen bonding pattern in the other form defines a sheet-like structure. Because the anhydrous material is both acidic and hygroscopic.

Oxalic acid is a relatively strong acid, despite being a carboxylic acid.



Oxalic acid acidity is 1.2. Oxalate, the conjugate base of oxalic acid, is an excellent ligand for metal ions. At optimum pH (2.5-3), the dissolution of iron pure hematite (Fe_2O_3) (105-140 μm) follows a diffusion control shrinkage. The dissolution was found to be very slow at 25-60°C but its rate increased rapidly above 90°C [30]. The reaction of conjugate base of oxalic acid, with iron oxide in silica sand mould, depends on pH value and temp. of the mould. The intense reaction takes place on a control pH (2.5-3) and specific temp. >90°C. At these specific conditions during casting, the oxalic acid may leach the iron oxide present in the moulding sand. Presence of iron oxide in moulding sand assures high thermal stability and hot strength. Reduction of iron oxide decreases the mechanical resistance and permeability of moulding sand.

Oxalate has been used to dissolve the iron oxide from various sources. As dissolution required a controlled pH for maximum reaction it is essential to create a hydroxide – oxalate mixture for use in leaching process. The characteristic of NaOH, KOH- and NH_4OH – Oxalic acid mixture show that due to precipitation of salts like $\text{Na}_2\text{C}_2\text{O}_4(s)$ and $\text{NaHC}_2\text{O}_4(s)$, the sodium hydroxide oxalic acid could act as pH buffer for leaching. Such precipitation also reduces the concentration of free bioxalate, HC_2O_4 required for dissolution of iron oxide [31]

The effect of acetic acid and carbonic acid on the clays in the soils has been studied by L.I.Tao and collaborators [24]. By changing thickness of electric double layer of soil grain diffusion and adsorbility of polar water molecule, the concentration of acetate or carbonic acid makes soil particles agglomerate or disperse and result in variation of plasticity and permeability of the compacted clay. By dissolving aluminium clay mineral, acetic acid increases the clay permeability and plasticity index. There is a chemical reaction of the carbon acid with the metal cation which can generate insoluble carbonates resulting in decrease of the clay liner permeability. It gives evidences for the clay liner stability. Microstructures of China clay treated with oxalic acid at 50X and SEM images (1000X) are given in fig. 13 & 14 respectively.

Conclusion

1. Generally the excess charge on the mineral is negative, and it attracts the cations from the solution to neutralize this charge.
2. Ion exchange capacity ranges in milliequivalents per 100 grams are kaolinite, 3-15 montmorillonite, 70-100 illite, 10-40. The common metallic cations found in exchange position in clay minerals are C^{++} , Mg^{++} , Na^+ and K^+ at low pH values H replaces the other cations.
3. The treatment of montmorillonite with mineral acids resulted in loss of lattice Al, Fe, and Mg, the amount removed depending upon acid concentration, temp. and time of contact. The three metal ions were removed in the same proportion that they occurred in mineral, indicating that acid treatment resulted in

complete decomposition on a part of clay. Silicon is not removed by the acid treatment.

4. Montmorillonite moderately treated with concentrated solution of mineral acid were largely hydrogen saturated when freshly prepared. On moist storage, however exchangeable hydrogen was lost and exchangeable Al appeared in its place. The rate at which H clays were spontaneously changed into the Al clays depends on the temp. and moisture of the content. At low temp. or low moisture content, H clays appeared to be fairly stable.
5. Phosphoric acid or its anions of its dissociation stick cementitously with the particles of sand (see text). They appear in rosette form or have scattered in irregular form. At high magnification cementitious zone are visible. The anions produced by the dissociation of phosphoric acid change the ions of first diffused layer to the normal ions of Mg^{++} , Ca^{++} , K^+ , Na^+ and hydrogen ions. Green sand moulding material based on chemical treatment show lower degree of mech. resistance and when it is dried by self hardening it shows high dry compression and shear strength. Phosphoric acid reacts with free ion and aluminum oxides present in clays, producing heat and rapid formation of insoluble hard cementitious products. The maximum time of hardening of core in air made by addition of phosphoric acid in core sand is recommended as 10-30 min.
6. It has been found that inorganic acid such as sulfuric acid and HCl easily contaminate the clay products with sulphate and chloride and therefore should be avoided as much as possible, on the other hand if oxalic acid is used, any acid left behind will be destroyed on heating or firing.
7. The oxalic acid dissolves the iron oxides present in the clay and in the silica sand used for making the mould material. However the reaction is found to be rapid on only above 90°C at 2.5 – 3 pH. Similarly tartaric acid does not produce any stable compound on dissociation. Its K, Na, Sb derivatives do not have any cementitious characteristics. They are in the form of cream. Its aqueous solution can only dissolve Cu (II) oxide layer. Tartaric acid is muscle toxin therefore it should be used carefully.

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Future Research

Reactivity of clay minerals with inorganic and organic acids, alkalis and salts has vastly been studied by the researchers working on this topic. Author desires that foundry men should further study the effects of these after their addition in the sand mould before pouring and after

complete solidification of the casting. Ultimately their effect on the mechanical resistance of the mould mixture can be determined and substantial limits of their amounts, which can produce best quality casting can be estimated. Oxalic acid is industrially utilized in leaching for removal of oxides of iron from the clays. This effect may also be further studied for moulding sands based on clays.

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