

Chemistry of Ferric Sulphate in Pulpotomy – Monograph

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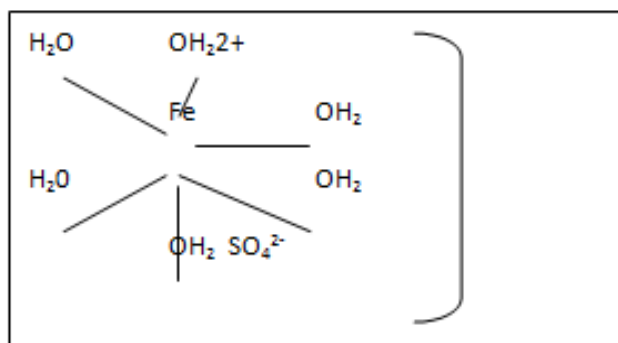
I. Introduction

Pulpotomy is a technique that has been used to treat primary teeth of which only the coronal pulp has been affected or infected by caries or traumatized while the radicular pulp remains healthy⁽¹⁾ The success of pulpotomy may be increased by promoting homeostasis of the remaining pulpal tissue. This procedure can be done to both primary and permanent teeth. The most commonly used medicaments for pulpotomy are Ferric Sulphate, mineral trioxide aggregate and calcium hydroxide

Ferric sulphate

Ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$), is a chemical compound which is said to be the sulphate of trivalent iron. It is usually yellow, rhombic crystalline salt and soluble in water at room temperature. It is used in dyeing as a mordant and as a coagulant for industrial wastes. It is used as an astringent and styptic. Ferric sulphate, can be used to arrest any bleeding from the pulp prior to the placement of medicament. Ferric sulphate ($\text{Fe}_2[\text{SO}_4]_3$) as a 15.5% solution (AstringentTM, Ultradent Products, Inc., Salt Lake City, UT), has been used commonly as a coagulative and homeostatic retraction agent for crown and bridge impressions and is slightly acidic. The mechanism of action of ferric sulphate is still debated, but agglutination of blood proteins results from the reaction of blood with both the ferric and sulphate ions.⁽²⁾

Ferric sulphate is used for gingival retraction before impression taking and in endodontic surgery for haemorrhage control. In contact with blood, a ferric ion protein complex is formed and the membrane of this complex seals the cut blood vessels mechanically thus producing hemostasis. An advantage of ferric sulphate is that less time is needed for procedures. When compared to formocresol, ferric sulphate does not have any bad smelling for the patients and the clinician⁽⁴⁾



Components of ferric sulphate:

The molecular formula of Ferric Sulphate is $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. The components of Ferric Sulphate are sulphuric acid which is $1\text{mg}/\text{m}^3$ and ferric sulphate which is $1\text{mg}/\text{m}^3$ Fe. The molecular weight of ferric sulphate is $399.858\text{gm}/\text{mol}$. The IUPAC name for Ferric Sulphate is Iron (3+); trisulphate. The valency for ferric sulphate is (3+), where ferric denotes valency as 3+ whereas ferrous denotes 2+

Chemical properties of ferric sulphate:

Ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, is readily obtained in the anhydrous condition by heating the nonhydrate to about 175°C ., or by heating ferrous or any of the ferric ammonium sulphates for prolonged periods in the presence of ammonium sulphate.

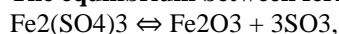
A convenient method of preparing anhydrous ferric sulphate consists in boiling 10 grams of ferrous sulphate with 100 c.c. of concentrated sulphuric acid for about an hour. When cold the bulk of the acid is poured off, the remainder being washed away with alcohol and finally with anhydrous ether. The salt is dried in an oven till constant weight is attained. Pickering found that it was necessary, in order to effect the complete removal of

excess of sulphuric acid, to heat until the product assumes a light brown colour while hot, becoming pink on cooling, the colour being due to the presence of traces of ferric oxide.

It is, when pure, a white powder, slowly soluble in water, yielding a deep brown solution.

When heated, ferric sulphate dissociates into ferric oxide, sulphur trioxide, sulphur dioxide, and oxygen, equilibrium being established if the operation is carried out in a closed vessel.

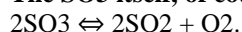
The equilibrium between ferric sulphate and its decomposition products is given by the equation: -



and the variation of the gaseous pressure with temperature is given by the expression: -

$$\log p = 11.8626 - 44720/4.584T.$$

The SO₃ itself, of course, partly dissociates, equilibrium being established according to the equation: -



p therefore represents the total pressure of all three gases, and T lies between 638° and 721°C.

At lower temperatures the pressures are as follow: -

Temperature. °C.	Pressure, mm.
599	53
630	102.5

When heated to 530° C. in open air, ferric sulphate decomposes completely, leaving a residue of ferric oxide. Several hydrates are known. The trihydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$, is obtained as a yellow mass on dehydrating the nonahydrate at about 100° C. In alcohol it dissolves readily, yielding a solution from which barium chloride is unable to precipitate the SO₄ as barium sulphate. It is believed, therefore, that the composition of the salt is more correctly represented by the formula $\text{Fe}_2(\text{SO}_3)_3 \cdot (\text{OH})_6$, analogous in constitution to the green chromium sulphate pentahydrate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$. It combines with two molecules of ethyl alcohol to form the compound $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{OH})_4 \cdot (\text{OC}_2\text{H}_5)_2$, the ethoxy groups replacing two hydroxyl groups.

The nonahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, occurs in nature as coquimbite in hexagonal prisms, and as rhombic crystalline plates under the name of Janosite. It may be prepared in the laboratory by evaporating a solution of ferric hydroxide in excess of sulphuric acid, and taking to dryness, when a mixture of normal and acid sulphates is produced. Upon exposure to moist air, and subsequent washing with alcohol, the nonahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, is obtained as violet hexagonal plates, density 2.116. Recoura describes a second variety of this salt, which results on allowing the above yellow salt to stand in a moist atmosphere for several days. Its empirical composition appears to be the same.

The decahydrate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$, occurs in nature as quenstedtite, in monoclinic crystals, the crystallographic elements being: -
a: b: c = 0.3940: 1: 0.4058. $\beta = 78^\circ 7.5'$.

It is obtained as the stable solid in contact with acidified solutions of ferric sulphate containing from 25 to 28 per cent, of SO₃, or by the combined action of nitric and sulphuric acids on ferrous sulphate.

Ferric sulphate is slowly soluble in water, and dissolves more readily in the presence of ferrous sulphate, but its solubility is lowered by addition of aluminium sulphate.

The densities of various concentrations of the salt in water at 17.5° C. are given as follow: -

Fe ₂ (SO ₄) ₃ (per cent.)	10	20	30	40	60
Density	1.0854	1.1825	1.3090	1.4506	1.8006

A neutral solution of ferric sulphate upon concentration does not deposit crystals of the nonahydrate, but a mixture of yellowish green copiapite, and the white acid sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$. Upon dilution, ferric sulphate solutions readily undergo hydrolysis, precipitates being obtained which, however, have no well-defined composition. A study of the electric conductivities of aqueous solutions of the salt indicates that the hydrolysis proceeds in two stages, embodying (1) a rapid change unaccompanied by precipitation, and (2) a slower change, progressing at a measurable rate, and accompanied by the production of a so-called basic salt. Colloidal ferric hydroxide does not appear to be formed during hydrolysis, the salt thus differing from ferric chloride and nitrate.

Ferric sulphate also undergoes hydrolysis when its solution is boiled with potassium iodate and iodide. Thus: -
 $\text{Fe}_2(\text{SO}_4)_3 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 3\text{K}_2\text{SO}_4 + 3\text{I}_2$.

In dilute solution ferric sulphate is reduced by metallic iron to ferrous sulphate. In contact with platinum the velocity of the reaction is increased, but rise of temperature has the reverse effect.

Copper is readily dissolved by ferric sulphate solution, and the action is not affected by light. The reaction is practically instantaneous on the surface of the metal, so that the observed velocity in the solution is governed by the rate of stirring.

Ferric sulphate is insoluble in concentrated sulphuric acid and in concentrated hydrochloric acid.

A solution of ferric sulphate in 90 per cent, sulphuric acid forms an intense red solution with nitric oxide, probably due to formation of a complex salt of formula $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{NO}$, which, however, has not been isolated.

Ferric sulphate in solution possesses a remarkable power of combining with animal or vegetable substances, and it cannot be extracted from the combination by hydrochloric acid. Barium chloride solution may be boiled with the compound without undergoing any change. Meat treated with ferric sulphate solution retains its red colour, but becomes exceedingly hard, so that it can hardly be scratched with the finger-nail.

Numerous basic salts occur in nature, chief amongst which areamarantite, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$; fibro-ferrite, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 10\text{H}_2\text{O}$; castanite, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 8\text{H}_2\text{O}$; a copiapite, $3\text{Fe}_2\text{O}_3 \cdot 8\text{SO}_3 \cdot 27\text{H}_2\text{O}$ or $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 18\text{H}_2\text{O}$, and planoferrite, $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 15\text{H}_2\text{O}$.

Botryogen contains ferrous and magnesium oxides associated with ferric sulphate, thus: $\text{FeO} \cdot \text{MgO} \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

A basic sulphate, of formula $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ or $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{Fe}_2\text{O}_3$, is precipitated from dilute solutions of ammonium iron alum upon prolonged standing, but no basic sulphates are formed by mixing ferric sulphate solutions with freshly precipitated ferric hydroxide. On heating ferric sulphate solution in sealed tubes at 150°C . and 275°C . respectively, crystalline products have been obtained, corresponding to the formulae $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $10\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$.

A basic ferric sulphate under the name of chemical sand is used commercially to neutralise the alkali present in waste soap lyes from which the glycerine is to be recovered. It is manufactured by mixing dry and finely powdered iron ore (oxide) with concentrated sulphuric acid, and allowing the fluid mass to spread out on an iron floor. When solidification has taken place, the mass is broken up and heated at a temperature of 200° to 280°C . for some hours, when it is ready for use, and consists essentially of ferric oxide and ferric sulphate.

An acid sulphate, termed ferric tetra sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$, may be obtained by dissolving the anhydrous sulphate in 10-normal sulphuric acid, and allowing the white crystalline product to dry. It is produced, together with a copiapite, when a neutral solution of ferric sulphate is concentrated. It is soluble in water, and decomposes at 100°C . The sulphuric acid may be replaced by sulphates of the alkali and other metals yielding well-defined compounds, for which reason the salt is frequently termed ferricdisulphuric acid, the formula being expressed as $\text{H}[\text{Fe}(\text{SO}_4)_2] \cdot 4\text{H}_2\text{O}$. When exposed over concentrated sulphuric acid it slowly loses five molecules of water, yielding $2\text{H}[\text{Fe}(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O}$, the same change taking place rapidly at 98°C .(3,4)

II. Conclusion

Ferric sulphate promotes pulpalhaemostasis through a chemical reaction with blood and forms a protective metal-protein clot over the underlying vital radicular pulp. Only less time is consumed in treating with ferric sulphate as a medicament which is a major advantage in pulpotomy. Thus, it is the most acceptable variation of the traditional application times of these medicaments in pulpotomy.

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