"how to make" paste for plates in "lead acid" battery

http://en.wikipedia.org/wiki/Lead-acid_battery#Plates

The Faure pasted-plate construction is typical of automotive batteries. Each plate consists of a rectangular lead grid alloyed with antimony or calcium to improve the mechanical characteristics. The holes of the grid are filled with a mixture of red lead and 33% dilute sulphuric acid. (Different manufacturers have modified the mixture). The paste is pressed into the holes in the plates which are slightly tapered on both sides to assist in retention of the paste. This porous paste allows the acid to react with the lead inside the plate, increasing the surface area many fold. At this stage the positive and negative plates are similar, however expanders and additives vary their internal chemistry to assist in operation when in use. Once dry, the plates are then stacked together with suitable separators and inserted in the battery container. An odd number of plates is usually used, with one more negative plate than positive. Each alternate plate is connected together. After the acid has been added to the cell, the cell is given its first forming charge. The positive plates gradually turn the chocolate brown colour of lead dioxide, and the negative turn the slate gray of 'spongy' lead. Such a cell is ready to be used. Modern manufacturing methods invariably produce the positive and negative plates ready formed, so that it is only necessary to add the sulphuric acid and the battery is ready for use.

One of the problems with the plates in a lead-acid battery is that the plates change size as the battery charges and discharges, the plates increasing in size as the <u>active material</u> absorbs <u>sulfate</u> from the acid during discharge, and decreasing as they give up the sulfate during charging. This causes the plates to gradually shed the paste during their life. It is important that there is plenty of room underneath the plates to catch this shed material. If this material reaches the plates a shorted cell will occur.

The paste material used to make battery plates also contains carbon black, blanc fixe (barium sulfate) and *lignosulfonate* (a particular version used is made by the vanallin process, which is resulfonated derivative of lignosulfonate that is alkaline oxidized, hydrolyzed, partially desulfonated). The blanc fixe acts as a seed crystal for the lead to lead sulfate reaction. The blanc fixe must be fully dispersed in the paste in order for it to be effective. The lignosulfonate prevents the negative plate from forming a solid mass of lead sulfate during the discharge cycle. It enables the formation of long needle like crystals. The long crystals have more surface area and are easily converted back to the original state on charging. The carbon black increases the formation speed during the "curing" of the battery. Lignosulfonates inhibit the formation of the battery plate. The carbon black counteracts this problem. It has been found that sulfonated naphthalene condensate dispersant is a more effective expander than lignosulfonate and can be used to speed up the formation of the battery plate. This dispersant is believed to function to improve dispersion of barium sulfate in the paste, reduce hydroset time, produce a stronger plate which is resistant to plate breakage, to reduce fine lead particles and thereby improve handling and to improve pasting characteristics. It extends the life of the

battery by increasing the end of charge voltage. The sulfonated naphtahlene condensate polymer dispersant can be used in about one-half to one-third the amount of lignosulfonate and is stable to higher temperatures than lignosulfonate^[1]

About 60% of the weight of an automotive-type lead-acid battery rated around 60 Ah (8.7 kg of a 14.5 kg battery) is lead or internal parts made of lead; the balance is electrolyte, separators, and the case. ^[2]

[edit] Separators

Separators are used between the positive and negative plates of a lead acid battery to prevent short circuit through physical contact, mostly through <u>dendrites</u> ('treeing'), but also through shedding of the active material.

Separators obstruct the flow of ions between the plates and increase the internal resistance of the cell.

Various materials have been used to make separators:

- wood
- rubber
- glass fiber mat
- cellulose
- sintered PVC
- microporous PVC/polyethylene.

An effective separator must possess a number of mechanical properties; applicable considerations include permeability, porosity, pore size distribution, specific surface area, mechanical design and strength, electrical resistance, ionic conductivity, and chemical compatibility with the electrolyte. In service, the separator must have good resistance to acid and oxidation. The area of the separator must be a little larger than the area of the plates to prevent material shorting between the plates. The separators must remain stable over the operating temperature range of the battery.

Wooden separators were orignally used, but deteriorated in the acid electrolyte. Rubber separators were stable in the battery acid.

Lead dioxide

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Lead dioxide		
IUPAC name	lead(IV) oxide	
Other names	plumbic oxide	
Identifiers		
CAS number	[1309-60-0]	
Properties		
Molecular formula	PbO ₂	
Molar mass	239.2 g/mol	
Except where noted otherwise, data are given for materials in their <u>standard state</u> (at 25 °C, 100 kPa) Infobox references		

Lead(IV) oxide, PbO₂, also **plumbic oxide** and **lead dioxide**, is an <u>oxide</u> of <u>lead</u>, with lead in <u>oxidation state</u> +4. It has a molar mass of 239.2 g/mol. It occurs in nature as the mineral <u>plattnerite</u>.

When hydrated, it forms plumbic hydroxide or lead(IV) hydroxide, Pb(OH)₄; given the formula, this is a mainly hypothetical compound.

Lead dioxide is <u>amphoteric</u>. Lead dioxide can dissolve in strong base to form <u>plumbate</u> ion, $Pb(OH)_6^{2^-}$. This can then form plumbate compounds. In acid conditions, it is

typically reduced to lead(II) ion, Pb^{2+} ; lead(IV) ion, Pb^{4+} , is not found in <u>aqueous</u> <u>solution</u>.

The most important use of lead dioxide is as the cathode of <u>lead acid batteries</u>. This arises from the anomalous metallic conductivity of PbO_2 —TiO₂, ZrO₂, GeO₂, and SnO₂ are all insulators with a band gap around 3eV, however PbO_2 is a metallic conductor. This is thought to be due to anionic vacancies in the structure creating a formally mixed valent lead oxidation state.

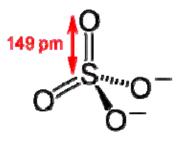
A <u>lead acid</u> battery is based on the equilibrium between lead metal and lead dioxide in <u>sulfuric acid</u>.

 $Pb + PbO_2 + 2HSO_4^- + 2H^+ \rightarrow 2PbSO_4 + 2H_2O, E = +2.05 V$

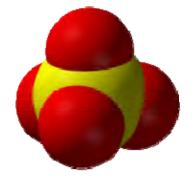
Sulfate

From Wikipedia, the free encyclopedia

Jump to: <u>navigation</u>, <u>search</u> "So4" redirects here. For the rotation group, see SO(4).



The structure and bonding of the sulfate ion



Space-filling model of the sulfate ion

In <u>inorganic chemistry</u>, a **sulfate** (<u>IUPAC</u>-recommended spelling; also **sulphate** in <u>British English</u>) is a <u>salt</u> of <u>sulfuric acid</u>.

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[edit] Chemical properties

The sulfate ion is a <u>polyatomic anion</u> with the <u>empirical formula</u> $SO_4^{2^-}$ and a molecular mass of 96.06 <u>daltons</u>; it consists of a central <u>sulfur atom</u> surrounded by four equivalent oxygen atoms in a <u>tetrahedral</u> arrangement. The sulfate ion carries a negative two <u>charge</u> and is the <u>conjugate base</u> of the <u>bisulfate</u> (or hydrogen sulfate) ion, HSO_4^- , which is the conjugate base of H₂SO₄, <u>sulfuric acid</u>. Organic sulfates, such as <u>dimethyl sulfate</u>, are covalent compounds and <u>esters</u> of sulfuric acid.

[edit] Preparation

Methods of preparing ionic sulfates include:^[1]

- dissolving a metal in sulfuric acid
- reacting sulfuric acid with a metal hydroxide or oxide
- oxidizing metal <u>sulfides</u> or <u>sulfites</u>

[edit] Properties

Many examples of ionic sulfates are known, and many of these are highly <u>soluble</u> in <u>water</u>. Exceptions include <u>calcium sulfate</u>, <u>strontium sulfate</u>, lead (II) sulfate, and <u>barium sulfate</u>, which are poorly soluble. <u>Radium sulfate</u> is the most insoluble sulfate known. The barium derivative is useful in the <u>gravimetric analysis</u> of sulfate: one adds a solution of, perhaps, <u>barium chloride</u> to a solution containing sulfate ions. The appearance of a white precipitate, which is <u>barium sulfate</u>, indicates that sulfate anions are present.

The sulfate ion can act as a ligand attaching either by one oxygen (monodentate) or by two oxygens as either a <u>chelate</u> or a bridge.^[11] An example is the neutral metal complex

 $PtSO_4P(C_6H_5)_{32}$ where the sulfate ion is acting as a bidentate ligand. The metal-oxygen bonds in sulfate complexes can have significant covalent character.

[edit] Structure and bonding

The S-O bond length of 149 pm is shorter than expected for a S-O single bond. For example, the bond lengths in <u>sulfuric acid</u> are 157 pm for S-OH. The tetrahedral geometry of the sulfate ion is as predicted by <u>VSEPR theory</u>.

The first description of the bonding in modern terms was by <u>Gilbert Lewis</u> in his groundbreaking paper of 1916 where he described the bonding in terms of electron octets around each atom, i.e. no double bonds and a <u>formal charge</u> of 2+ on the sulfur atom.^[2]

Later, Linus Pauling used <u>valence bond theory</u> to propose that the most significant resonance canonicals had two π bonds (see above) involving d orbitals. His reasoning was that the charge on sulfur was thus reduced, in accordance with his <u>principle of electroneutrality</u>.^[3] The double bonding was taken by Pauling to account for the shortness of the S-O bond (149 pm).

Pauling's use of d orbitals provoked a debate on the relative importance of π bonding and bond polarity (electrostatic attraction) in causing the shortening of the S-O bond. The outcome was a broad consensus that d orbitals play a role, but are not as significant as Pauling had believed.^{[4][5]} A widely accepted description involves $p\pi - d\pi$ bonding, initially proposed by D.W.J Cruickshank, where fully occupied p orbitals on oxygen overlap with empty sulfur d orbitals (principally the d_z^2 and d_x^2 .²).^[6] In this description, while there is some π character to the S-O bonds, the bond has significant ionic character. This explanation is quoted in some current textbooks.^{[7][1]} The Pauling bonding representation for sulfate and other main group compounds with oxygen is a common way of representing the bonding in many textbooks.^{[7][1]}

[edit] Uses

Sulfates are important in both the chemical industry and biological systems:

- The <u>lead-acid battery</u> typically uses sulfuric acid.
- Some anaerobic microorganisms, such as those living near deep sea <u>thermal vents</u> use sulfates as electron acceptors.
- <u>Copper sulfate</u> is a common <u>algaecide</u>.
- <u>Magnesium sulfate</u>, commonly known as <u>Epsom salts</u>, is used in therapeutic baths.
- <u>Gypsum</u>, the natural <u>mineral</u> form of hydrated <u>calcium sulfate</u>, is used to produce <u>plaster</u>.
- The sulfate ion is used as <u>counter ion</u> for some <u>cationic</u> drugs.

[<u>edit</u>] History

Some sulfates were known to alchemists. The vitriol salts, from the Latin *vitreolum*, glassy, were so-called because they were some of the first transparent crystals known.^[8] <u>Green vitriol</u> is ferrous sulfate heptahydrate, FeSO₄·7H₂O; <u>blue vitriol</u> is copper sulfate pentahydrate, CuSO₄·5H₂O and <u>white vitriol</u> is zinc sulfate heptahydrate, ZnSO₄·7H₂O. <u>Alum</u>, a double sulfate with the formula $K_2Al_2(SO_4)_4·24H_2O$, figured in the development of the chemical industry.

[edit] Environmental effects

Sulfates occur as microscopic particles (<u>aerosols</u>) resulting from <u>fossil fuel</u> and <u>biomass</u> combustion. They increase the acidity of the <u>atmosphere</u> and form <u>acid rain</u>.

[edit] Main effects on climate

The main direct effect of sulfates on the climate involves the scattering of light, effectively increasing the Earth's <u>albedo</u>. This effect is moderately well understood and leads to a cooling from the negative <u>radiative forcing</u> of about 0.5 W/m² relative to pre-industrial values,^[9] partially offsetting the larger (about 2.4 W/m²) warming effect of greenhouse gases. The effect is strongly spatially non-uniform, being largest downstream of large industrial areas.

The first indirect effect is also known as the <u>Twomey effect</u>. Sulfate aerosols can act as <u>cloud condensation nuclei</u> and this leads to greater numbers of smaller droplets of water. Lots of smaller droplets can diffuse light more efficiently than just a few larger droplets.

The second indirect effect is the further knock-on effects of having more cloud condensation nuclei. It is proposed that these include the suppression of drizzle, increased cloud height, ^[10] to facilitate <u>cloud</u> formation at low <u>humidities</u> and longer cloud lifetime.^[11] Sulfate may also result in changes in the particle size distribution, which can affect the clouds radiative properties in ways that are not fully understood. Chemical effects such as the dissolution of soluble gases and slightly soluble substances, surface tension depression by organic substances and accommodation coefficient changes are also included in the second indirect effect.^[12]

The indirect effects probably have a cooling effect, perhaps up to 2 W/m^2 , although the uncertainty is very large. Sulfates are therefore implicated in <u>global dimming</u>, which may have acted to offset some of the effects of <u>global warming</u>.

[edit] Other sulfur oxoanions

Molecular formula Name

SO ₅ ²⁻	Peroxomonosulfate
${\rm SO_4}^{2-}$	Sulfate
SO ₃ ²⁻	<u>Sulfite</u>
$S_2O_8^{2-}$	Peroxodisulfate
S ₂ O ₇ ²⁻	Pyrosulfate
$S_2O_6^{2-}$	Dithionate
$S_2O_5^{2-}$	<u>Metabisulfite</u>
$S_2O_4^{2-}$	Dithionite
$S_2O_3^{2-}$	<u>Thiosulfate</u>
$S_4 O_6^{2-}$	<u>Tetrathionate</u>

Lignosulfonates

From Wikipedia, the free encyclopedia

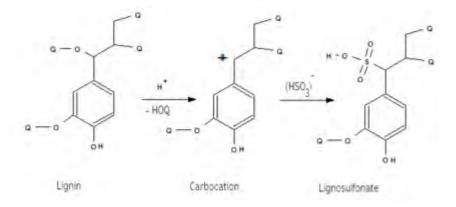
(Redirected from <u>Lignosulfonate</u>) Jump to: <u>navigation</u>, <u>search</u>

Lignosulfonates, or **sulfonated lignin**, (<u>CAS number</u> 8062-15-5) are water-soluble anionic <u>polyelectrolyte polymers</u>: they are byproducts from the production of <u>wood pulp</u> using <u>sulfite pulping</u>.^[1]

Most delignification in sulfite pulping involves acidic cleavage of <u>ether</u> bonds, which connect many of the constituents of <u>lignin</u>.^[2] The <u>electrophilic carbocations</u> produced during ether cleavage react with bisulfite ions (HSO₃⁻) to give sulfonates.

$$R-O-R' + H^+ \rightarrow R^+ + R'OH$$
$$R^+ + HSO_3^- \rightarrow R-SO_3H$$

The primary site for ether cleavage is the α -carbon (carbon atom attached to the aromatic ring) of the <u>propyl</u> (linear three carbon) side chain. The following structures do not specify the structure since lignin and its derivatives are complex mixtures: the purpose is to give a general idea of the structure of lignosulfonates. The groups labeled "Q" can be a wide variety of groups found in the structure of lignin. Sulfonation occurs on the side chains, not on the aromatic rings, like in <u>p-toluenesulfonic acid</u>.



Lignosulfonate have very broad ranges of <u>molecular mass</u> (they are very <u>polydisperse</u>). A range of from 1000–140,000 <u>da</u> has been reported for softwood lignosulfonates with lower values reported for hardwoods.^[11]

[edit] Preparation

Lignosulfonates are recovered from the spent pulping liquids (red or brown liquor) from sulfite pulping. The most widely used industrial process is the Howard process, in which 90–95% yields of calcium lignosulfonates (CAS number 904-76-3), are precipitated by adding of excess <u>calcium hydroxide</u>. Ultrafiltration and ion-exchange can also be used to separate lignosulfonates from the spent pulping liquid.^[11] A list of CAS numbers for the various metal salts of lignosulfonate is available.^[3]

[edit] Uses

Lignosulfonates have a wide variety of applications.^[4]

The single largest use for lignosulfonates is as <u>plasticizers</u> in making <u>concrete</u>,^[1] where they allow concrete to be made with less water (giving stronger concrete) while

maintaining the ability of the concrete to flow. Lignosulfonates are also used during the production of <u>cement</u>, where they act as grinding aids in the <u>cement mill</u> and as a <u>rawmix</u> slurry <u>deflocculant</u> (that reduces the <u>viscosity</u> of the slurry).

Lignosulfonates are also used for the production of <u>plasterboard</u> to reduce the amount of water to, make the <u>stucco</u> flow, and form the layer between to sheets of paper. This allows lower kiln temperatures to dry the plasterboard and to save energy.

The ability of lignosulfonates to reduce the viscosity of mineral slurries is used to advantage in <u>oil drilling mud</u>, where it replaced <u>tannic acids</u> from <u>quebracho</u> (a tropical tree).

Lignosulfonates are used to disperse <u>pesticides</u>, <u>dyes</u>, ^[5] <u>carbon black</u>, ^[6] and other insoluble solids and liquids into water. They are used in <u>tanning leather</u>. They are also used to suppress dust on unpaved roads. ^[7]

<u>Oxidation</u> of lignosulfonates from <u>softwood</u> trees produced <u>vanillin</u> (artificial vanilla flavor), but this is not a current use.^[8]

<u>Dimethyl sulfide</u> and <u>dimethyl sulfoxide</u> (an important organic <u>solvent</u>) are produced from lignosulfonates. The first step involves heating lignosulfonates with <u>sulfides</u> or elemental <u>sulfur</u> to produce dimethyl sulfide. The <u>methyl</u> groups come from methyl <u>ethers</u> present in the lignin. Oxidation of dimethyl sulfide with <u>nitrogen dioxide</u> produces dimethyl sulfoxide (DMSO).^[1]

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Sulfite process

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The **sulfite process** produces <u>wood pulp</u> which is almost pure <u>cellulose</u> fibers by using various <u>salts</u> of <u>sulfurous acid</u> to extract the <u>lignin</u> from wood chips in large pressure vessels called <u>digesters</u>. The salts used in the pulping process are either <u>sulfites</u> $(SO_3^{2^-})$, or <u>bisulfites</u> (HSO_3^{-}) , depending on the <u>pH</u>. The counter <u>ion</u> can be <u>sodium</u> (Na^+) , <u>calcium</u> (Ca^{2+}) , <u>potassium</u> (K^+) , <u>magnesium</u> (Mg^{2+}) or <u>ammonium</u> (NH_4^+) .

The first <u>pulp mill</u> using the sulfite process was built in <u>Sweden</u> in 1874 and used magnesium as the <u>counter ion</u>.^[11] Calcium became the standard counter ion until the 1950s. Sulfite pulping was the dominant process for making wood pulp intil it was surpassed by the <u>kraft process</u> in the 1940s. Sulfite pulps now account for less than 10% of the total chemical pulp production.^[11]

The sulfite process is <u>acidic</u> and one of the drawbacks is that the acidic conditions <u>hydrolyze</u> some of the cellulose, which means that sulfite pulp fibers are not as strong as kraft pulp fibers. The <u>yield</u> of pulp (based on wood used) is higher than for kraft pulping and sulfite pulp is easier to <u>bleach</u>. Apart from printing and specialty papers, a special grade of sulfite pulp, known as "<u>dissolving pulp</u>" is used to make cellulose derivatives.^[2] <u>Lignosulfonates</u> are an important byproduct of sulfite bleaching.^[3] These materials are used in making <u>concrete</u>, <u>drilling mud</u>, <u>drywall</u> and so on.

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[edit] History

The use of wood to make pulp for paper began with the development of <u>mechanical</u> <u>pulping</u> in <u>Germany</u> by <u>F.G. Keller</u> in the $1840s^{[4]}$. Chemical processes quickly followed,

first with J. Roth's use of <u>sulfurous acid</u> to treat wood, followed by <u>B. Tilghman's US</u> <u>patent</u> on the use of <u>calcium bisulfite</u>, Ca(HSO₃)₂, to pulp wood in 1867.^[1] Almost a decade later the first commercial <u>sulfite pulp mill</u> was built in <u>Sweden</u>. It used magnesium as the counter ion and was based on work by <u>Carl Daniel Ekman</u>. By 1900 sulfite pulping had become the dominant means of producing wood pulp, surpassing mechanical pulping methods. The competing chemical pulping process, the sulfate or <u>kraft process</u> was developed by <u>Carl F. Dahl</u> in 1879 and the first <u>kraft mill</u> started (in Sweden) in 1890.^[1] The invention of the <u>recovery boiler</u> by <u>G.H. Tomlinson</u> in the early 1930s ^[4] allowed kraft mills to recycle almost all of their pulping chemicals. This, along with the ability of the kraft process to accept a wider variety of types of wood and produce stronger fibers ^[5] made the kraft process the dominant pulping process starting in the 1940s.^[1] Sulfite pulps now account for less than 10% of the total <u>chemical pulp</u> <u>production^[1]</u> and the number of <u>sulfite mills</u> continues to <u>decrease</u>.^{[6][7][8]}

[edit] Current status

Sulfite pulp remains an important <u>commodity</u>, especially for specialty papers and as a source of cellulose for non-paper applications. Sulfite pulp is used to make fine paper, tissue, <u>glassine</u>.^[9] and to add strength to <u>newsprint</u>. A special grade of bleached sulfite pulp is known as "<u>dissolving pulp</u>"^[2] which is the raw material for a wide variety of cellulose derivatives, for example <u>rayon</u>, <u>cellophane</u>, <u>cellulose acetate</u> and <u>methylcellulose</u>. Rayon is a reconstituted cellulose fiber used to make many fabrics. Cellophane is a clear reconstituted cellulose film used in wrapping and windows in envelopes. Cellulose acetate was used to make flexible films for photographic use, computer tapes and so on and also to make fibers. Methylcellulose and other cellulose ether derivatives are used in a wide range of everyday products from <u>adhesives</u> to <u>baked goods</u> to <u>pharmaceuticals</u>.^[10]

[edit] Processes involved in sulfite pulping

[edit] Pulping liquor preparation

The pulping liquor for most sulfite mills is made by burning <u>sulfur</u> with the correct amount of <u>oxygen</u> to give <u>sulfur dioxide</u>, which is then absorbed into water to give <u>sulfurous acid</u>.

$$\begin{split} & S + O_2 \rightarrow SO_2 \\ & SO_2 + H_2O \rightleftharpoons H_2SO_3 \end{split}$$

Care must be taken to avoid the formation of <u>sulfur trioxide</u> since it gives undesired <u>sulfuric acid</u> when it is dissolved in water.

$$2 \text{ SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$$
$$\text{SO}_3 + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{SO}_4$$

Sulfuric acid is undesirable since it promotes hydrolysis of cellulose without contributing to delignification.

The cooking liquor is prepared by adding the counter ions as hydroxides or carbonates. The relative amounts of each species present in the liquid depned largely on the relative amounts of sulfurous used. For monovalent $(Na^+, K^+ \text{ and } NH_4^+)$ hydroxides, MOH:

 $\begin{array}{l} H_2SO_3 + MOH \rightarrow MHSO_3 + H_2O \\ MHSO_3 + MOH \rightarrow M_2SO_3 + H_2O \end{array}$

For divalent (Ca^{2+} , Mg^{2+}) carbonates, MCO_3 :

 $\begin{array}{l} MCO_3+2H_2SO_3 \rightarrow M(HSO_3)_2+CO_2+H_2O\\ M(HSO_3)_2+MCO_3 \rightarrow 2\ MSO_3+CO_2+H_2O \end{array}$

[edit] Pulping

Sulfite pulping is carried out between pH 1.5 and 5, depending on the counterion to sulfite (bisulfite) and the ratio of base to sulfurous acid. The pulp is in contact with the pulping chemicals for 4 to 14 hours and at temperatures ranging from 130 to $160 \stackrel{\circ}{\underline{C}}$ (266 to 320 $\stackrel{\circ}{\underline{F}}$), again depending on the chemicals used.

Most of the intermediates involved in delignification in sulfite pulping are <u>resonance-stabilized carbocations</u> formed either by protonation of carbon-carbon double bonds or acidic cleavage of ether bonds which connect many of the constituents of lignin. It is the latter reaction which is responsible for most lignin degradation in the sulfite process.^[4] The <u>electrophilic</u> carbocations react with bisulfite ions (HSO₃⁻)to give sulfonates.

 $\begin{array}{l} R\text{-}O\text{-}R'+H^{+}\rightarrow R^{+}+R'OH\\ R^{+}+HSO_{3}^{-}\rightarrow R\text{-}SO_{3}H \end{array}$

The sulfite process does not degrade <u>lignin</u> to the same extent that the <u>kraft process</u> does and the <u>lignosulfonates</u> from the sulfite process are useful <u>byproducts</u>.

[edit] Chemical recovery

The spent cooking liquor from sulfite pulping is called <u>brown</u> or <u>red liquor</u> (compared to <u>black liquor</u> in the kraft process). Pulp washers, using <u>countercurrent</u> flow, remove the spent cooking chemicals and degraded lignin and hemicelulose. The extracted brown liquor is concentrated, in <u>multiple effect evaporators</u>. The concentrated brown liquor can be burned in the <u>recovery boiler</u> to generate steam and recover the inorganic chemicals for reuse in the pulping process or it can be neutralized to recover the useful byproducts of pulping.

Ammonia-based processes do not allow recovery of the pulping chemicals since ammonia or ammonium salts are oxidized to <u>nitrogen</u> and <u>nitrogen oxides</u> when burned.

The earliest process used calcium, obtained as inexpensive <u>calcium carbonate</u> and there was little incentive to recover the inorganic materials. Sodium-based processes use a recovery system similar to that used in the <u>kraft recovery process</u>, except that there is no "lime cycle".

The recovery process used in magnesium-based sulfite pulping the "Magnefite" process is well developed.^[11] The concentrated brown liquor is burned in a recovery boiler, producing <u>magnesium oxide</u> and <u>sulfur dioxide</u>, both of which are recovered from the flue gases. Magnesium oxide is recovered in a wet <u>scrubber</u> to give a <u>slurry</u> of <u>magnesium hydroxide</u>.

 $MgO + H_2O \rightarrow Mg(OH)_2$

This magnesium hydroxide slurry is then used in another scrubber to absorb <u>sulfur</u> <u>dioxide</u> from the flue gases producing a magnesium bisulfite solution that is clarified, filtered and used as the pulping liquor.

$$Mg(OH)_2 + 2 SO_2 \rightarrow Mg(HSO_3)_2$$

[edit] Byproducts

Sulfite pulping is generally less destructive than kraft pulping, so there are more usable byproducts. Chief among these are <u>lignosulfonates</u>, which find a wide variety of uses whereas relatively inexpensive agent is needed to make a water dispersion of a water-insoluble material. Lignosulfonates are used in <u>tanning</u> leather, making <u>concrete</u>, <u>drilling</u> <u>mud</u>, <u>drywall</u> and so on.^[3]

Oxidation of lignosulfonates was used to produce <u>vanillin</u> (artificial vanilla), but this process is no longer used.^[12]

Acid hydrolysis of cellulose during sulfite pulping produces <u>monosaccharides</u>, predominanently <u>mannose</u>,^[4] which can be fermented to produce <u>ethanol</u>.

[edit] See also

- Kraft process
- <u>Pulp mill</u>
- <u>Wood pulp</u>
- <u>Bleaching of wood pulp</u>
- <u>Paper</u>

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this: how can I make a lead dioxide cathode from lead dioxide powder? Also, is PbO2 a conductor; if not, how do I coat a conductor electrode like graphite with lead dioxide?

Why not coat a lead electrode with lead dioxide? The chemistry will happen at the surface. I would think that would happen naturally if you applied the proper potential at high pH. I don't know if it would be stable once you switched to sulfuric acid.

okay now, maybe if i changed the setup, and instead of actually making the electrodes, i simply perform the reaction:

 $Pb + PbO2 + 2HSO4 - \rightarrow 2PbSO4 + 2H2O$

I would use sheet lead, powder pbo2 and 6M sulphuric acid. What could I get out of this, both in terms of just the discharge reaction itself, and for the sulfation effect? Does it make sense to measure something like the enthalpy of the above reaction, then again with crystallised lead sulphate in it?

Have you read the Wiki on lead batteries? Lead oxide is pressed as a paste into lead electrodes to form the lead oxide part of the circuit. If you sprinkle lead oxide onto a lead plate you will likely see galvanic pitting but I don't know if you will know anything about the effect of electrode sulfation on the 'battery'.

hmm yeah i have read that... sorry to ask.. but what about the chemical reaction

 $Pb + PbO2 + 2HSO4 \rightarrow 2PbSO4 + 2H2O?$

Can I get anything out of that?

Yes, you will make additional lead sulfate up to the point of saturation. It will then begin to ppt on all surfaces if you have the proper amount of lead sulfate and sulfuric acid to start with and you use enough lead oxide. How will you visualize it? How will it be measured?

How to make a dry cell

Dry cells are one of the most commonly used household objects. We use dry cells in watches, torches, transistors, walkmans and even the remote controls of our TVs. Dry cells provide the necessary electricity required to power these devices. A normal dry cell is cylindrical in shape made of zinc. A carbon rod passes through its center and a paste of manganese dioxide and ammonium chloride surrounds this rod. When the both ends of the cell are z connected to a bulb through a wire, the bulb glows due to the flow of current. The voltage of such a cell is about 1.5 volt. Let us now make a dry cell at home.

Procedure

Make some starch paste by mixing some starch and water and then boiling it. Add sufficient quantity of manganese dioxide to the starch paste, making a very thick paste of manganese dioxide.

Spread this manganese dioxide paste evenly on the zinc plate. Now take some cotton wool and flatten it to fit the shape of the zinc plate. Soak this cotton wool in ammonium chloride solution. Now add another layer of manganese dioxide paste over the cotton wool.

Now put the carbon plate over this layer of manganese dioxide and your dry cell is ready to use.

To see the dry cell in action connect wires to the two ends of the bulb holder and connect the other ends of the wires to the carbon and zinc plates using metallic clips. The bulb begins to glow.

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