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THE HYDROUS OXIDES

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to the collodion for mantle coating to increase the protection given the mantle.[1]

The crystals of beryllia obtained from an electric arc furnace are almost as hard as corundum, and so it is sometimes mixed with other substances as an abrasive.[1] The oxide would also seem to possess certain advantages over magnesia as a refractory for crucibles. It has a high melting point, 2150°, and after calcination it resists acid corrosion much more effectively than magnesia.[2] The oxide has also shown some promise as a body in paints and in the manufacture of certain dental products and synthetic gems.

Hydrous Magnesium Hydroxide

Magnesium hydroxide in a flocculent hydrous condition is formed by the action of water on magnesia obtained from the naturally occurring carbonate, magnesia alba.[3] The precipitated mass is not a hydrous oxide as is so frequently the case, but is a hydrous hydrate[4] made up of very finely divided particles which adsorb alkali so strongly[5] that its presence prevents the adsorption of sulfate and chloride.[6] The oxide is more soluble when first formed, going over to a less soluble crystalline form quickly when the magnesium ion concentration is high, and more slowly when it is low.[7] X-radiograms show the microcrystalline particles to possess a structure identical with natural brucite.[8] Large crystals of the hydrate are formed by heating magnesium chloride with an excess of potash in a limited volume of water.[9]

The flocculent hydroxide dried over sulfuric acid at 100 to 200° adsorbs more than 1.5 H_2O, which it gives up in a dry atmos-

[1] *Cf.* James: *Metal Ind.*, **11**, 66 (1917).

[2] Berzelius: *Schweigger's J.*, **15**, 236 (1815); Lebeau: *Compt. rend.*, **123**, 818 (1896); *Ann. chim. phys.*, (7) **16**, 457 (1899).

[3] Deville: *Compt. rend.*, **61**, 975 (1865); Ditte: *Ibid.*, **73**, 191 (1871).

[4] Van Bemmelen: *J. prakt. Chem.*, **26**, 238 (1882).

[5] Grouvelle: *Ann. chim. phys.*, (2) **17**, 351 (1821); Marchand and Scheerer: *J. prakt. Chem.*, (1) **50**, 385 (1850).

[6] Patten: *J. Am. Chem. Soc.*, **25**, 186 (1903).

[7] Glaldbaek: *Z. anorg. Chem.*, **144**, 145, 269 (1925).

[8] Böhm and Niclassen: *Z. anorg. Chem.*, **132**, 6 (1924).

[9] De Schulten: *Compt. rend.*, **101**, 72 (1885).

phere.[1] The amount of adsorbed water taken up decreases with the temperature of ignition and the anhydrous oxide obtained at high temperatures hydrates very slowly. Campbell[2] burned magnesite between 600 and 800°, obtaining an impure oxide which hydrates completely in 3 days. Between 1000 and 1100°, the magnesia was said to undergo a change resulting in a marked decrease in the rate of hydration until at 1450°, about the temperature used in burning Portland cement, the oxide, immersed in water for 18 months, combines with 60 per cent of that necessary to form $MgO \cdot H_2O$. Le Chatelier[3] gave 1600° as the transformation temperature, and Parravano and Mazzetti[4] placed it at 800°, at the same time calling attention to the effect of impurities on the transformation temperatures; thus, ferric oxide hastens it. Mellor[5] pointed out the absence of a definite transformation temperature and showed the change to proceed more quickly the higher the temperature of calcination. Mellor attributed the change to a conversion from amorphous to crystalline periclase; but this cannot be the case, as Hedvall[6] found the oxide formed at various temperatures to have a cubic-lattic crystal structure which underwent no change on heating. The specific gravity of calcined magnesia varies, however, between 3.0 and 3.6, depending not only on the method of preparation but on the temperature of calcination. The low-temperature low-specific-gravity oxide not only reacts much more rapidly with water than the oxide formed at high temperatures, but the former possesses a greater adsorption capacity for gases and moisture, and dissolves more rapidly in acids.[7] Although the melting point of magnesia is in the neighborhood of 2500°, it undoubtedly sinters at a much lower temperature, and this change in physical character probably accounts for the difference in reactivity of the oxide ignited at different temperatures.

[1] Van Bemmelen: "Die Absorption," 369 (1910).

[2] *J. Ind. Eng. Chem.*, **1**, 665 (1909).

[3] *Compt. rend.*, **102**, 1243 (1883).

[4] *Atti accad. Lincei*, (5) **30 I**, 63 (1921).

[5] *Trans. Ceram. Soc.*, **16**, 85 (1917).

[6] *Z. anorg. Chem.*, **120**, 327 (1922).

[7] Ditte: *Compt. rend.*, **73**, 111, 191, 220 (1871); Anderson: *J. Chem. Soc.*, **87**, 257 (1905).

minute interlacing crystals[1] of what has been assumed to be basic chloride. People are unable to agree on the formula of the hypothetical salt, and it is probably only an indefinite solid solution of magnesium oxide and chloride. The chloride may be dissolved out completely with boiling water, leaving hard magnesium oxide. The cement can be prepared by adding water to a suitable mixture of dry components.[2] It possesses marked mechanical strength and is used for cementing glass and metal and for making artificial stones; *e.g.*, *xylolith* is made from sawdust, cement, and water.

The tendency of calcined magnesia to take up water and expand is of importance in the cement industry, since the presence of as much as 2 to 3 per cent of uncombined magnesia would give a concrete that would disintegrate from excessive expansion.[3]

In addition to the applications mentioned, hydrous magnesium hydroxide has been substituted for charcoal as a clarifier in the refining of sugar.[4] Its mild basic action has been utilized in pharmaceutical preparations as an antacid. Milk of magnesia is a fairly stable suspension of the hydrous oxide that is widely employed as a mouth wash; in the preparation of modified milk for infants; and in combating hyperacidity of the stomach.

Rhythmic Bands.—The precipitation of magnesium hydroxide in gelatin in the form of rhythmic bands has been investigated quantitatively by Popp.[5] When ammonia diffuses into gelatin containing magnesium chloride, it is found that with increasing concentration of magnesium salt, the rings increase in number and thickness, and the space between them decreases; with diminishing ammonia concentration, the rings decrease in number and thickness, and the space between them increases; adding ammonium chloride causes the number and thickness of the rings to decrease and the space between them to increase; with diminishing gelatin concentration, both the rings and the space between them increase, the number remaining the same. The rhythmic precip-

[1] LUHMANN: *Chem. Ztg.*, 25, 345 (1901); KRIEGER: *Ibid.*, 34, 246 (1910).

[2] *Cf.* KRANER: German Patent 143933 (1902); LYTE and TATTERS: British Patent 11545 (1890).

[3] CAMPBELL and WHITE: *J. Am. Chem. Soc.*, 28, 1273 (1906); CAMPBELL: *J. Ind. Eng. Chem.*, 1, 665 (1909).

[4] HAKE: *J. Soc. Chem. Ind.*, 2, 149 (1883).

[5] *Kolloid-Z.*, 36, 208 (1925).

itation takes place also in clay, agar, silica gel, fine sand, and glass beads in water. To account for these and other Liesegang phenomena, Wolfgang Ostwald[1] postulates the existence of three principal diffusion waves in all reacting systems giving typical periodic precipitates: The added electrolyte diffuses into the gel; the electrolyte in the gel diffuses outward; and the electrolyte produced by the reaction may diffuse in both directions. In many instances the soluble reaction product possesses a higher rate of diffusion than one or both of the reactants. Ostwald assumes further that many and probably all reactions giving Liesegang rings are balanced reactions. Precipitation, therefore, depends on certain critical concentrations of reactants which vary over wide ranges through the interference of diffusion waves. In support of the theory, it was shown that many Liesegang rings are destroyed by subsequent introduction, by diffusion, of the electrolyte produced in the reaction. Thus, bands of magnesium hydroxide are destroyed by allowing ammonium chloride to diffuse into the gel supporting them. The converse of rhythmic precipitation, namely rhythmic solution, may sometimes be produced by adding a reaction product. Thus a uniform precipitate of lead sulfate in gelatin gel containing ammonia is converted into rings by the interdiffusion of concentrated ammonium chloride. Continuous precipitation results if one reactant is replaced by a compound not giving a balanced reaction, as evidenced by the failure to get bands when alkali is substituted for ammonia in the precipitation of magnesium hydroxide in gelatin. The distribution of chloride ions in a gelatin jelly containing magnesium chloride was found after the diffusion of ammonia, to show periodic variation between values much higher and much lower than those in the original gel.

Wolfgang Ostwald's theory of rhythmic banding is merely an extension of Holmes'[2] diffusion theory based on Frick's law of diffusion. The influence of such phenomena as supersaturation,[3] peptization and coagulation of the precipitate,[4] adsorption

[1] *Kolloid-Z.* (*Zsigmondy Festschrift*). 36, 380 (1925).
[2] *J. Am. Chem. Soc.*, 40, 1187 (1918).
[3] OSTWALD: "Lehrbuch allgem. Chemie," 2d ed., 2, 778.
[4] FREUNDLICH: "Kapillarchemie," 2d ed., 1009 (1922); SEN and DHAR: *Kolloid-Z.*, 34, 270 (1924).

of reacting solutes by the precipitate,[1] etc. is looked upon as a secondary factor in the banding process.

Stable sols of hydrous magnesium hydroxide in water have not been prepared without the aid of a protective colloid; but a typical sol of great stability is formed by shaking magnesia with methyl alcohol.[2]

Hydrous Zinc Oxide

The voluminous precipitate obtained by adding the calculated amount of ammonia or alkali to a solution of zinc salt is hydrous zinc oxide, the amount of adsorbed water depending on the exact method of formation, the temperature, and the age of the sample.[3] If the precipitation is carried out at 100°, it contains less than 1 per cent of adsorbed water. Although the oxide newly formed in the cold is a transparent gel,[4] it quickly becomes flocculent and later powdery, the change being accompanied by a gradual transformation into the crystalline state.[5] The hydrous oxide ages more rapidly if precipitated from chloride rather than from nitrate; and in the presence of alkali rather than water. As in the case of hydrous beryllium oxide, the microcrystalline mass formed on standing in the cold always contains more water than corresponds to $ZnO \cdot H_2O$, and in this state, it is probably hydrous zinc hydroxide. Kaufmann[6] observed a gradual loss of water on heating a precipitated hydrous zinc oxide to 125°, where it had the composition $Zn(OH)_2$ which it maintained to 180°, and then broke down gradually, giving anhydrous ZnO at a low red heat. There are no hydrates of $Zn(OH)_2$, as assumed by De Forcrand[7] and Boedecker.[8]

[1] Bradford: *Biochem. J.*, **10**, 169 (1905).
[2] Neuberg and Rewald: *Kolloid-Z.*, **2**, 354 (1908).
[3] Goudriaan: *Rec. trav. chim.*, **39**, 505 (1920).
[4] Linder and Picton: *J. Chem. Soc.*, **61**, 130 (1892).
[5] Fricke and Ahrndts: *Z. anorg. Chem.*, **134**, 344 (1924); Fricke: *Ibid.*, **138**, 48 (1924); Böhm and Niclassen: *Ibid.*, **132**, 1 (1924).
[6] Dissertation, München, 69 (1913); *cf.* Pascal: *Compt. rend.*, **177**, 765 (1923).
[7] *Compt. rend.*, **135**, 36 (1902).
[8] *Liebig's Ann. Chem.*, **94**, 358 (1855).