

CONDUCTIVITY OF AQUEOUS DUST SOLUTIONS

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ABSTRACT

This paper presents an analysis of the conductivity of aqueous solutions of dusts occurring in the atmosphere, stressing the effect on [overhead] high voltage insulation. Based on some references, a list of chemical compounds occurring in dusts is presented. The reason for nonlinearity of the relation between the conductivity of dust solutions and their dilution is discussed. The effect of dust solubility on the conductivity is described. A specification of the weakly soluble chemical compounds, together with the conductivity of their saturated solutions, is given.

INTRODUCTION

Due to the pollution of the atmosphere by dusts, foreign solid particles are deposited on the surfaces of insulators. In conditions of increased humidity and rain, this leads to the formation of a layer of electrolytic solution, characterized by high conductivity. This is the cause of the contamination hazard to overhead insulators. Growing conductivity of the contaminant (a given thickness) leads to a decrease of the voltage strength of the insulation. Thus, the properties of aqueous dust solutions, combined with the level of dust emission, are the basis of classifying the terrain into "pollution zones". The discussed properties often differ significantly from those of the simple electrolyte solutions, e.g. NaCl or CaCl₂, used for modeling the pollution in laboratories.

CHEMICAL COMPOSITION OF DUSTS

Atmospheric dusts consist of solid particles of varied dispersion, which depends on their type and distance to the nearest emitters. Large particles are dominant in the vicinity of emitters, while the fine particles (below 45 μm) are spread by winds over large distances.

In industrial emission, three types of dust are dominant: those formed by the combustion and processing of coal (electric plants, boilers, coke ovens), metallurgical (smelting plants), and dolomite-lime (cement mills, building industry). Non-organized dumps and fly-sands are also sources of emission.

The metal content of dusts in the Cracow district is shown in Table 1. Among the alkaline metals Ca, Mg, K, Na prevail, and among the heavy metals Fe, Mn, Zn, Pb, and Cu.

Table 1

Maximum content of metals in the industrial dusts of the Cracow agglomeration during 1983.

The type of dust	Content of metals								
	Ca	Fe	Mg	Mn	Na	K	Zn	Pb	Cu
coal combustion	2,8	4,5	1,2	0,1	0,1	0,7	1500	220	140
metallurgical	7,3	4,5	4,1	1,5	0,3	0,4	21000	2600	390
dolomite-lime	4,5	3,9	1,1	2,9	1,2	2,3	14000	1900	170

The dusts contain compounds of varied solubility: the insoluble oxides (SiO₂, Fe₂O₃, Al₂O₃) and sulphides (CuS, PbS, FeS), weakly soluble carbonates (CaCO₃, MgCO₃), and fully soluble sulphates, nitrates, chlorides and hydroxides (CuSO₄, KNO₃, KCl, NaOH). Depending on the dominant component, aqueous dust solutions can be neutral, acidic, due to the presence of salts with hydrolyzed cations (NH₄Cl, FeCl, (NH₄)₂SO₄, NaHSO₄) or a slight content of acids: sulphuric, nitric, carbonic, or alkaline, due to the presence of hydroxides (Ca(OH)₂, KOH, NaOH) or salts with hydrolyzed anions (Na₂CO₃, KS, CH₃COONa).

The chemical composition of dusts at different locations, as given in the literature, is shown in Table 2. The insoluble compounds, SiO₂, Al₂O₃, Fe₂O₃, are the most common. There occur some strongly soluble salts: NaCl, NaNO₃, MgSO₄ and others. One should note the relatively high content of weakly soluble calcium sulphate.

Table 2

Chemical composition of dusts at various locations.

Miechowice Electric Plant, Poland								
Chemical compound	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
% weight	48,5	26	12,7	4,7	4,7	1,3	0,7	1,6
Sylmar Converter Station, California								
Salt	Ca(NO ₃) ₂	NaNO ₃	Zn(NO ₃) ₂	NaCl	MgSO ₄	CaSO ₄	K ₂ SO ₄	Ca ₃ PO ₄
% weight	42,3	8	8,7	13,2	4,2	15,3	7,8	0,5
Dusts from a Pakistani desert								
Salt				NaCl	CaCO ₃	CaSO ₄	other	
% weight				42	23	25	10	

COMPARISON BETWEEN THE CONDUCTIVITIES OF AQUEOUS DUST SOLUTIONS AND THE ELECTROLYTES

The conductive properties are characterized by the relation between the conductivity and the concentration of the substance in solution. The Debye-Hückel theory explains the relation between the concentration and the equivalent conductivity of strong and medium strong electrolytes, contained in the dust. The theory assumes complete dissociation of a strong electrolyte in solution and evaluates only the electrostatic interaction between ions. The decrease of equivalent conductivity is described by

$$\Lambda = \Lambda_0 - a\sqrt{I} \tag{1}$$

in which Λ is the equivalent conductivity, Λ_0 the limiting equivalent conductivity, a a constant parameter, dependent on the temperature and the type of electrolyte, and I the ion strength of the solution, given as half the sum of the products of all ion concentrations C_i multiplied by their squared electric charge Z_i .

$$I = \frac{1}{2} \sum_i c_i z_i^2 \tag{2}$$

In case of the simple, type 1-1, electrolytes (KCl, NaCl), the ion strength of a solution is equal to the molar concentration. In Figs. 1 and 2, the relation (1) has been drawn for some acids, bases and salts, based on the data given in the physical chemistry tables [5].

Industrial dusts form a mixture of many chemical substances, only partly soluble in water. The conductivity of dust increases with the content of the soluble components. This is an important factor in assessing the insulation contamination hazard [6].

The relations between the conductivity of aqueous dust solutions and their concentration in water are given in Fig. 3. The mass of dust (both the soluble and insoluble components) contained in 100 g of distilled water is indicated on the abscissa. The marked nonlinearity of the characteristics, observed in the 2000 $\mu\text{S}/\text{cm}$ range, cannot be explained by the decrease of equivalent conductivity. For comparison, the conductivity of 90% SiO₂, 10% MgSO₄ mixture has been drawn on the same Figure. It indicates only slight nonlinearity, much smaller than in the case of the

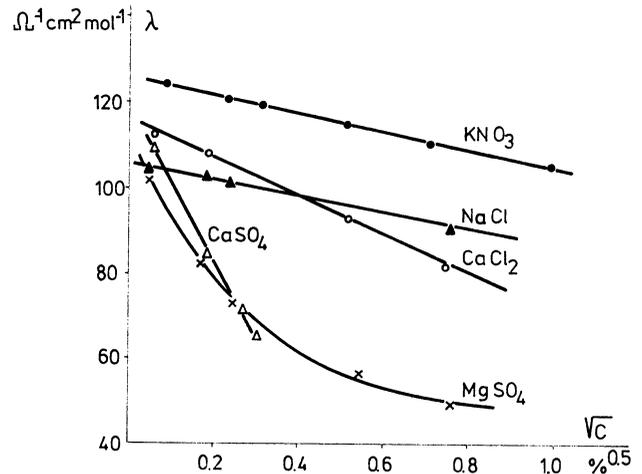


Fig. 1: Relation between the equivalent conductivity of salt solutions and their concentration.

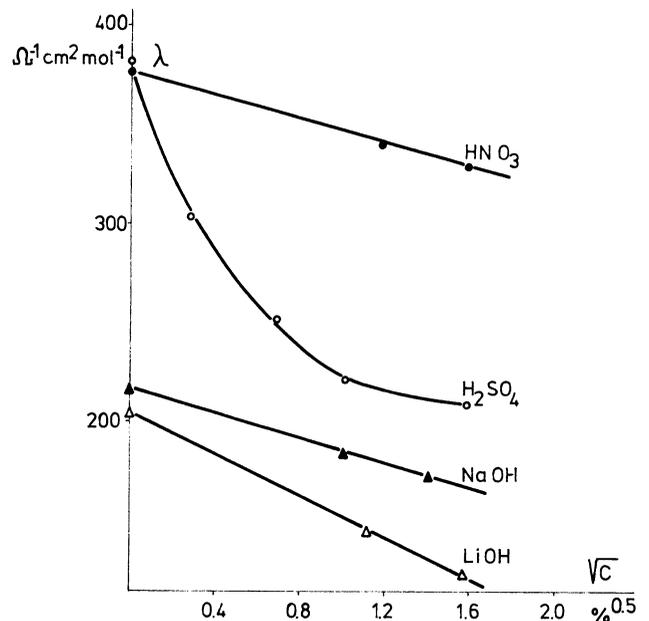


Fig. 2: Relation between the equivalent conductivity of acidic and basic solutions and their concentration.

industrial dusts. The impact of decreasing equivalent conductivity of acids and bases is even smaller, e.g. 1% NaOH solution which has a conductivity of 46 mS/cm, is characterized by only 15% drop in the ionic mobility (Fig. 2). A significant property can be observed in case of the solution of dust from an electric plant, powered by lignite. The conductivity has a break-point at some value of dust content in water. This suggests that the solubility has a distinct effect on the mechanism of conductivity of the tested solutions.

To test this hypothesis, the mass of components dissolved in water has been determined for a range of dust content. This relation is given in Fig. 4. The similarity of the curves of conductivity and dissolved mass proves that the conductivity is approximately proportional to the concentration of the solution in the

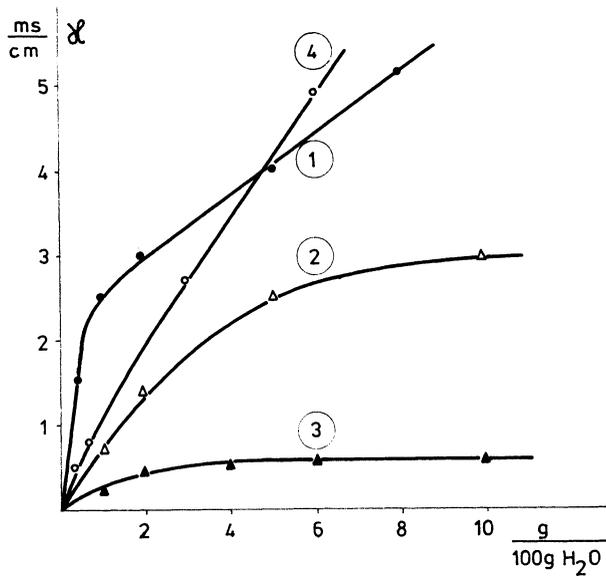


Fig. 3: Relation between the conductivity of aqueous dust solutions and their concentration in water: 1 - dusts from an electric plant heated with lignite, 2 - dusts from a copper smelting plant, 3 - dusts from a cement mill, 4 - mixture of 10% MgSO₄ with 90% SiO₂.

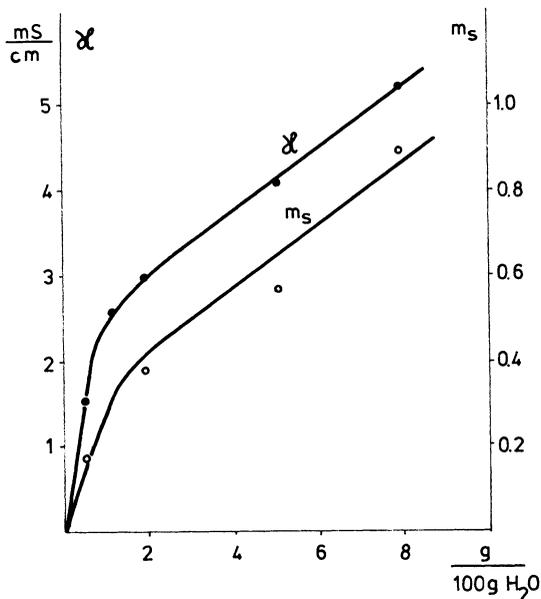


Fig. 4: Conductivity κ and the mass of dissolved components m_s in relation to the dust content in water.

tested range. The influence of decreasing equivalent conductivity is much smaller than that of solubility.

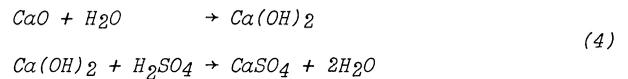
$$\kappa \approx A C \quad (3)$$

where κ is the conductivity, A the ratio of proportionality, and C the concentration.

The importance of solubility is even more noticeable in the case of dusts emitted by cement mills (Fig. 3, curve 3). On reaching a concentration of 6 g in 100 g H₂O, the conductivity of the solution does not increase any more, having a stable value of only 550 μ S/cm.

WEAKLY SOLUBLE CHEMICAL COMPOUNDS

Curve 1 in Fig. 3 suggests that the limit of solubility of a dominant component in the dusts is reached at the value of conductivity 2500 μ S/cm. Chemical analysis of the dusts has indicated that the content of calcium surpasses 10%. Among the calcium compounds only one - calcium sulphate, CaSO₄ - can cause this nonlinearity. Its solubility is 0.089 g in 100 g H₂O and its saturated solution has a conductivity of about 2000 μ S/cm. The samples of dust had been taken in the vicinity of cooling towers, which emit a large quantity of sulphuric acid dissolved in water drops. The content of CaSO₄ may be enriched by the following reactions:



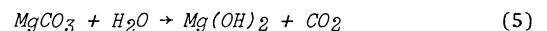
in which CaSO₄ is the product of neutralizing the sulphuric acid by slaked lime. A large content of lime in the fly-ash (Table 2) as well as the emission of SO₂ and the effect of acidic rains account for the general occurrence of these reactions.

Besides the calcium sulphate, other weakly soluble salts have an effect on the conductive properties of dust solutions. The conductivities of the saturated solutions of weak soluble electrolytes are given in Table 3. Solubilities have been calculated, using the solubility product, based on data from [7,8] or taken from data in [9]. Conductivity of the saturated solutions has been measured experimentally and verified by comparing with the theoretical values obtained from the equivalent conductivity and solubility. The compound MgCO₃ was found to have a distinct property. Its solubility is similar to CaSO₄, but it is hydrolyzed and transformed into the much less soluble magnesium hydroxide

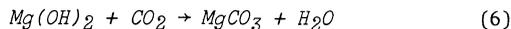
Table 3

Solubility and conductivity of the aqueous solutions of poorly soluble electrolytes at 18°C.

Chemical compound	Logarithm of the solubility product	Solubility mg/100g H ₂ O	Conductivity of saturated solution μ S/cm
CaSO ₄	- 4,37	89	2000
Ca(OH) ₂	- 5,03	160	7500
Ca/HCO ₃ /2		12	420
CaCO ₃	- 8,41	0,63	30
MgCO ₃	- 4,05	80	750
Mg/HCO ₃ /2		24	2800
Mg(OH) ₂	- 10,9	1,4	200
MgC ₂ O ₄	- 4,1	30	200



In turn Mg(OH)₂ reacts with carbon dioxide dissolved in water, again forming magnesium carbonate



Conductivity of the weakly soluble magnesium hydroxide in technically pure water reaches 200 $\mu\text{S/cm}$, even though the theoretical value, calculated from the solubility product, is only 87 $\mu\text{S/cm}$. The solubility of weakly soluble electrolytes depends on a number of general factors influencing dissociation, as well as on such specific ones as the electrolyte ions being involved in other reactions taking place in the solution. The most important factors, influencing the solubility of residues, are the influence of shared ions, the influence of salts, having no common ion with the residue (so-called salting effect), the influence of the pH of the solvent, hydrolysis of the residue, the impact of complexing, and the influence of the temperature and the state of the residue. Therefore, the solubility of dust is not simply the sum-total of solubilities of the components.

The observed conductive properties of dusts are very important in everyday practice. They explain why there is no correlation between the parameters describing the contaminant deposit on the insulator, i.e. the surface conductivity and the equivalent salt deposit density ESDD. The relation between the surface conductivity and ESDD, for three different contaminants, is shown in Fig. 5. In the case of NaCl deposits this is a straight line, while in the case of the industrial dusts the curves are similar to lines 1 and 2 in Fig. 3. The measurement of surface conductivity is realized after spraying the insulator with a slight amount of water, limited by drop formation. On the other hand, ESDD is determined after washing the insulator with a greater amount of distilled water. The content of dust in water is then much smaller than after spraying.

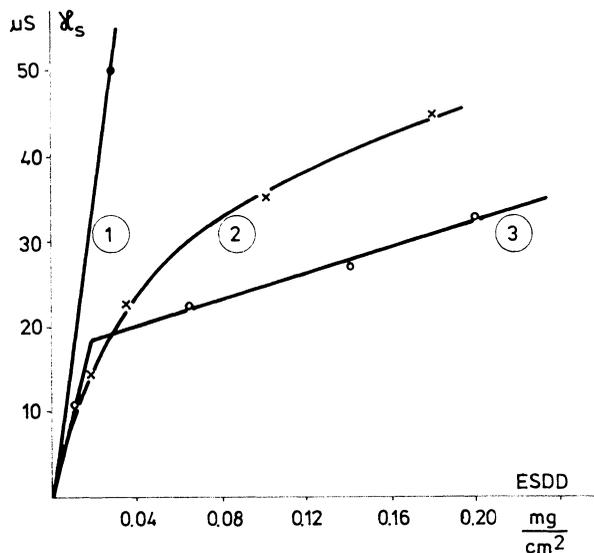


Fig. 5: Surface conductivity κ_s as a function of ESDD for 1 - a layer of NaCl, 2 - a contaminant deposit from a copper smelting plant, 3 - a contaminant deposit containing a large percentage of CaSO_4 .

CONCLUSIONS

The effect of limited solubility of dust components on the conductive properties of aqueous solutions is much larger than that of decreased mobility of carriers in the concentrated solutions.

Calcium sulfate and other weakly soluble salts can play an important part in the mechanism of conductance in the aqueous solutions of industrial dusts.

The use of ESDD as a parameter of contamination hazard should be limited to dusts containing only strongly soluble components (having a linear relation between conductivity and dust content in water). The above conclusion significantly limits the permissible use of ESDD.

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