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Inorganic anion exchangers

A E Kapustin
Mariupol Metallurgical Institute

ABSTRACT. Data on inorganic substances showing basic and anion-exchange properties have been reviewed. The structural dependence of the number and strength of the basic centres has been discussed.

The bibliography contains 162 references.

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I. Introduction

Ion exchange materials are widely used in the most varied spheres of human activity. Ion exchange processes are acquiring particular importance in attempts to create waste-free technologies and closed technological schemes.

The need to prepare and purify water, to purifiy effluents and air from harmful impurities, and to obtain pure substances has for the last 50 years stimulated the development of research in the field of ion exchange and the production of new ion exchangers. The development of the industrial production of various ion exchangers has been no less intensive. There has been an extremely rapid increase in the number of publications on the synthesis and production of ion exchangers and the theory and practice of ion exchange, and a number of reviews have appeared.[1–3]

A basis for this rapid development has been provided by progress in the field of macromolecular compounds. The great majority of ion exchangers that have been studied, to say nothing of those used in industry, have been based on organic polymers.

It is appropriate to remember that the ion exchange process was first detected and studied in inorganic compounds—soils, earth, clays, and zeolites. A new stimulus to the development of ion exchange in inorganic materials was provided by progress in nuclear energy and radiochemistry. It became necessary to produce ion exchange materials with high stability to heat and radiation. It also became clear that the development of polymeric materials containing functional groups with a higher stability to heat and radiation is not promising,[4] since the stability of an ion exchanger is determined by the stability of the polymer matrix.[5]

Data on the properties of compounds such as aluminosilicates, oxides, hydroxides, sulphides, phosphates, salts of heteropolyacids, ferrocyanides, graphite oxides, and complex hydrated oxides have now been accumulated and systematised.[6,7] Zeolite aluminosilicate ion exchangers have been particularly well studied.[8,9]

Zeolites and the other compounds listed above, however, are almost all acidic substances, that is they are cation exchangers. Inorganic anion exchangers are much less familiar, and there are no published data on their use in industry.

The aim of the present review was to systematise published data on inorganic anion exchangers.

II. Terminology

Traditionally,[10–12] an "anion exchanger" is an ion exchanger containing fixed ions (or ionogenic groups) and exchanging anions. An ion exchanger is a two-phase heterogenous system, capable of dissociation and containing fixed ions, etc.

This definition is not comprehensive, however. In general, all anion exchangers are solid bases (ion exchangers in the salt form can be regarded as potential solid bases). The term solid base can be applied to a substance which is a proton acceptor or an electron donor.[13]

We shall use the term anion exchanger to describe a solid insoluble substance which contains Brönsted or Lewis basic centres and which shows basic properties over a wide pH range. It is assumed that the basic form of an anion exchanger can be obtained from the salt form by ion exchange.

The complete characterisation of an anion exchanger should include the following parameters:

1, the total concentration (mmol g^{-1}) of basic centres relative to the highest theoretically possible value;

2, the concentration of basic centres on the surface of the anion exchanger and in its bulk;

3, the strength distribution of the basic centres;

4, the physicochemical properties (specific surface, pore volume and radius, chemical, thermal, and radiation stability, accessibility of the centres in relation to steric factors);

5, the ion exchange properties (the form of the isotherms, and selectivity coefficients and series).

III. Determination of the basic properties of anion exchangers

To obtain a picture of the basic properties of solids, it is necessary to know the total quantity, nature, and strength distribution of the basic centres.

A solid base can convert an adsorbed acidic molecule into the conjugate base form. The basic centre may be a proton acceptor, taking them from the adsorbed molecule (Brönsted basic centre) or an electron donor, transferring them to the adsorbed molecule (Lewis basic centre).

The most complete information on the state of a surface is given by the indicator method. When an electrically neutral acidic indicator in a non-polar solvent is adsorbed on a solid base, the colour of the indicator changes to that characteristic of the conjugate base form. This indicates the presence of centres whose basic strength is sufficient to transfer electrons to the acid molecule.

By successively adsorbing indicators with different pK_a values on fresh specimens it is possible to obtain a qualitative picture of the basic strength distribution.

The concentration of basic centres (usually expressed in millimoles per unit weight or unit surface area) is determined quantitatively by titrating a suspension of the powdered solid base in a non-polar solvent with an acid solution. The quantity of acid required to convert the indicator into the acidic form corresponds to the number of basic centres whose basic strength is lower than pK_a for the indicator used in the titration. By using a range of indicators it is possible to obtain the distribution of the number of centres with respect to basic strength (Table 1).

Table 1. Indicators used to obtain information on the basic properties of solids.[7]

Indicator	Colour		pK_a
	acidic form	basic form	
Bromothymol Blue	yellow	green	7.2
2,4,6-Trinitroaniline	"	orange	12.2
2,4-Dinitroaniline	"	violet	15.0
4-Chloro-2-nitroaniline	"	orange	17.2
4-Nitroaniline	"	"	18.4
4-Chloroaniline	colourless	pink	26.5

The main disadvantage of the indicator method is that the basic strength is measured in a given specific medium, and with change in the conditions, both the concentration and the distribution of the basic centres may be quite different. Moreover, the large indicator molecules cannot penetrate to the centres inside fine pores.[9] This last restriction does not appear to be significant, however, since it is more important that the basic centres be accessible to the acid titrant, and to observe the indicator change the quantity adsorbed on the outer surface is sufficient. Thus the results obtained by titrating mercarbides with benzoic acid in the presence of Bromothymol Blue are close to those obtained by other methods, although this indicator cannot penetrate into the mercarbide pores.

A more significant limitation of the indicator method is that it cannot be used to determine the basic properties of solid anion exchangers in forms other than the hydroxide form. If the Brönsted centres are in the hydroxide form, the indicator method gives the total Brönsted and Lewis basic strength; otherwise, it gives only the Lewis basic strength.

Titration using aqueous solutions of acids makes it possible to determine the total quantity of basic centres, and Brönsted centres present in salt forms can also be titrated. Here it is necessary to be sure that the affinity of the titrant acid for the anion is appreciably greater than its affinity for the counter-ion, otherwise an equilibrium is established, and the number of centres found in this way is too low. In this case, naturally, the concentration of anions in the solution, and not the change in the pH of the medium, is followed.

In the titration with acid it is necessary to be certain that the solid framework does not break down.

The concentration of Brönsted basic centres on the surface of a solid can be estimated from data on exchange between the hydroxide groups of the surface and the anions from salt solutions.

If the number of centres is being determined for a new substance, it is necessary to carry out at least several measurements with different solutions containing different ions, since the selectivity of anion exchangers may be different.

This method can sometimes be used to determine the number of centres in a solid in different anion forms; here, the limitations are the same as those for aqueous titration with acids.

Calorimetric titration can be used to determine the basic strength by observing the increase in temperature due to the liberation of heat in the reaction of the anion exchanger with an acid in the liquid phase.

When gravimetric methods are used, gaseous acidic compounds such as phenol and carbon dioxide are used as adsorbates. After adsorption at a given pressure and temperature, the acid is desorbed from the anion exchanger, and the quantity of desorbed acid determined by DTA [12] or chromatography.[11]

Calorimetric and gravimetric methods can be used to find the quantity of Lewis basic centres and Brönsted centres in the OH form. Gravimetric methods also give a qualitative picture of the strength distribution of the centres, which can be made the basis of quantitative calculations.[11,12]

Important information on the basic strength of anion exchangers could be obtained by spectral methods. The spectra (infrared, ultrviolet, EPR) of acidic substances adsorbed on anion exchangers can be used to determine the nature of their interaction with the basic centres. The reactions of adsorbed molecules with Lewis basic centres and with hydroxide groups should give different spectra. There are no published data, however, on the spectroscopic study of the basic properties of solids.

Thus there is at present no general method for determining the nature, strength, and number of basic centres in all cases. The situation is particularly complicated if the anion exchanger is in the salt form. For a complete estimation of the basic strength of anion exchangers it is necessary to use several methods in succession. The study of the basic properties of solids should include the following stages:

1, conversion of the anion exchanger to the OH form (the degree of conversion can be followed, for example, by elemental analysis);

2, determination of the total basic strength by one of the methods;

3, determination of the Brönsted basic strength by one of the methods;

4, determination of the strength distribution of the basic centres by the indicator method;

5, conversion of the Brönsted centres to the salt form (with determination of the degree of conversion);

6, determination of the distribution of Lewis basic centres by the indicator method;

7, determination of the strength distribution of the Brönsted basic centres from the data balance.

The number of basic centres is expressed in mol g^{-1} or equiv g^{-1}; we shall use the dimensions given in the original works.

The great majority of inorganic anion exchangers are products of isomorphous replacement in the crystal lattice. The replacement of one element by another in a higher oxidation state leads to the production of an excess positive charge, whose compensation requires an anion. This structure is shown by many compounds which at present are assigned to different classes: mixed hydroxides, cyanides, insoluble salts, and inverse zeolites. We shall retain the traditional classification, although the above compounds have many similar properties; in particular, they show similar structure–property relationships.

IV. Double hydroxides

Double hydroxides form the most widespread class of inorganic anion exchangers. A very large number of representatives of this class are known, and they have been studied in considerable detail and are beginning to be used in industry. Related to the hydroxides is the class of mixed oxides, since most double oxides are obtained from double hydroxides and, most importantly, the oxides formed by heating double hydroxides with basic properties may also have a considerable number of basic centres. Moreover, it is impossible to draw a distinct boundary between oxides and hydroxides, or for that matter between mixed oxides and salts.

The discovery that preciptitating metal hydroxides form a mixture of solutions of the salts gives a new double hydroxide phase with anion exchange properties[13,14] was followed by further studies in this direction.[15–19]

For convenience, double hydroxides can be divided into three groups:

1, hydroxides formed by metal ions whose oxidation states differ by 1, for example $Ca_2Al(OH)_7$;

2, hydroxides in which the oxidation states of the metals differ by more than 1, for example $LiAl_2(OH)_7$;

3, hydroxides in which the metals have the same oxidation state, for example $MgNi(OH)_4$.

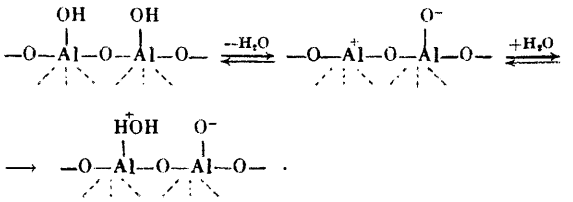
There also exist more complex hydroxides containing three or more metal cations with different oxidation states,[20] but these can be regarded as combinations of the above double hydroxides.

The structure and basic properties of complex hydroxides are best studied by regarding them as synthetic analogues of anionic clays. All clays are layer compounds made up of metal oxides. For example, clays of the simples type (kaolins) contain two layers: a tetrahedral silicate layer and an octahedral aluminate layer. At the edges and corners of each layer there are hydroxide groups, which on immersion in a salt solution can exchange with anions, but exchange between protons and various cations is also possible. Since cation exchange and anion exchange take place on the same groups, the exchange capacity of kaolins is approximately the same for cations and anions.[6]

Since clay minerals and double and other hydroxides have terminal hydroxide groups, they all are both cation exchangers and anion exchangers, and their ion exchange properties are determined primarily by the pH of the medium:

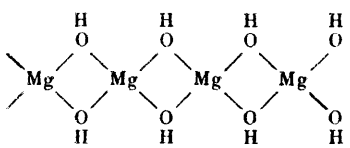
$$M^+ + OH^- \rightleftharpoons MOH \rightleftharpoons MO^- + H^+$$
$$pH<7 \qquad pH>7 .$$

The exchange capacity of ion exchangers in which exchange takes place on terminal groups is extremely low, and proportional to the surface area. The basic strength of these neutral hydroxides can be increased by covering the acidic centres, for example with water:[7]

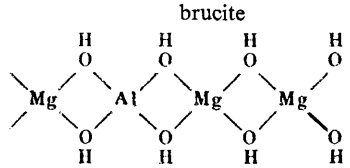


The ion exchange capacity of hydroxides increases considerably on isomorphous replacement of the metal cations. For example, the cation exchange capacity of layers of the type present in kaolins can be increased considerably by replacing Al^{3+} cations in the octahedral layer by Mg^{2+} or Fe^{2+}, and by replacing the Si^{4+} cations in the tetrahedral layer by Al^{3+}. The layers acquire a negative charge, which is compensated by alkali and alkaline earth metal cations situated between the layers, and also by solvating water molecules. These cations can be replaced by others, and this is responsible for the cation exchange properties of clay minerals. The ion exchange capacity depends on the extent of the isomorphous replacement, and in most cases it is much greater than that due only to exchange at edges and corners. Anionic clay minerals are mostly synthetic, but they are also found in nature.

Hydroxides with anion exchange properties can also be obtained by the isomorphous replacement of the cations of the basic layers. Naturally, in this case the oxidation state of the replacing cations must be greater than that of the replaced cations. For example, hydrotalcite can be obtained by the isomorphous replacement of Mg^{2+} ions by Al^{3+} ions in brucite.[15]



brucite



hydrotalcite

From the same elements it is possible to obtain both a cation exchanger and an anion exchanger. The isomorphous replacement of Mg ions by Al ions produces an excess positive charge, and therefore gives a substance anion exchange properties, and the replacement of Al ions in $Al(OH)_3$ by Mg gives cation exchangers. Thus it is always possible to calculate the degree of replacement of ions giving the greatest anion exchange capacity. This degree of replacement usually also corresponds to the most stable structure $M^{I}_{x}M^{II}_{y}(OH)_x$. The weakest basic centres are those in complex hydroxides containing metals with the same oxidation state. Their strength is determined only by the weak inductive influence due to the displacement of the electron density.

Mixed hydroxides can be prepared by different methods. The most frequently employed and well developed method is by precipitating the hydroxides from salt solutions.[21–31] Liquid-phase methods for synthesising anionic hydroxides have been reviewed.[15] From the advantages and disadvantages examined,[15] the following method, close to the optimal, was proposed for synthesising anionic hydroxides. A solution of the metal salts with concentrations of about 100 g litre^{-1}, taken in stoichiometric proportions, is added with stirring to a solution containing an approximately two-fold excess of alkali and carbonates (final pH 8–10). The precipitate is crystallised with heating for not less than 18 h. The higher the temperature and the longer the crystallisation time, the higher the quality of the product. At low temperatures, undesirable secondary phases may be formed.[32]

The properties of the hydroxides obtained, in particular their ion exchange properties, may be influenced by the nature of the precipitant and solution, the rate of precipitation, the nature of the salts used, the intensity of stirring, and various other factors. By varying these parameters it is possible to increase the yield of the desired product, to improve its properties, and, which is most important, to avoid the formation of secondary phases. Solutions of KOH, NaOH, Na_2CO_3, or ammonia are used as precipitants. Their selection requires justification. For example, the presence of super-stoichiometric quantities of sodium hydroxide increases considerably the range of crystallisation of double calcium aluminium hydroxide sulphate as a result of a decrease in the range of crystallisation of aluminium hydroxide.[33] Further increase in the concentrations of lithium, sodium, or potassium, however, may lead to breakdown of the compound obtained and conversion of the components into different phases.[34]

Not all double hydroxides can be obtained using strongly basic precipitants. Double copper aluminium hydroxides are formed only in hydroxide carbonate solutions, since at high pH values copper is precipitated as hydroxide carbonates.[35] Precipitation by ammonia is of limited application, because of possible complex formation.

The pH of the solution has a marked influence on the precipitation of hydroxides; the rate of precipitation and the stability of the compounds formed generally increase with increase in pH,[36] but on the other hand the selectivity of the process decreases. The formation of double hydroxides and their salts may take place over a period of several months or even years.[37] The highest selectivity is achieved by precipitating with dilute solutions of alkali or ammonia, taken in stoichiometic quantities.[38]

The formation of double hydroxides by precipitating with ammonia shows interesting features.[39] In the preparation of double hydroxides of zinc and chromium it was found that increase in temperature from 20 °C to 60 °C leads to the appearance of various secondary phases, both as a result of their parallel formation and as a result of decomposition of the principal phase. The ratio of the reagents being precipitated has less influence on precipitate formation than the basic strength of the solution; at different pH values, precipitates with different atomic ratios Zn:Cr are obtained from solutions with the same composition. The ratio also depends on the rate of the process. In general, increase in temperature and decrease in the rate of the process lead to the formation of secondary phases as a result of more extensive hydrolysis.

Danilov and co-workers[39] observed an extremely interesting fact, namely that the selectivity of formation of double zinc chromium hydroxide nitrate increases sharply when a very small quantity of acetic acid is added to the reaction mixture. The authors cited give no explanation for this phenomenon; it is quite possible that acetate ions (or acetic acid itself) are applicator anions. This is also indicated by the fact that the precipitate does not contain amorphous zinc- and chromium-containing hydroxide phases.

Decrease in the concentrations of the salts being precipitated and of the precipitant is accompanied by an increase in the degree of solvation of the hydroxides obtained,[2] and this also influences their properties, including the ion exchange properties. If however the precipitate is subsequently subjected to ageing[40] or thermal treatment, then this factor has no significant influence.

The nature of the metal being precipitated determines the conditions for its precipitation. Thus under the same conditions, selective precipitation of double magnesium aluminium hydroxides takes place but the formation of mixed nickel and cobalt hydroxides is accompanied by the formation of $Ni(OH)_2$ and $Co(OH)_2$.[15]

It is considered that the ability of zinc to form double hydroxides is weak.[13] Nevertheless, mixed hydroxides based on zinc have been studied in detail.[41–46] Only synthetic hydrotalcite $[Mg_xAl_y(OH)_x].X_n$ has been more intensively studied than anionic hydroxides based on zinc. The great majority of double hydroxides that have been synthesised, studied, and described are compounds based on divalent and trivalent metals. Double hydroxides containing alkali metals (except lithium) have not been studied in such detail.

Table 2 lists double hydroxides containing M^I and M^{II} whose properties were studied in the works cited.

Table 2. Literature sources containing information on the methods and characteristics of the preparation of synthetic anionic double hydroxides.

M^{II}	M^I							
	Al	Cr	Fe	Sc	Zr	Zn	Co	In
Mg	+	[15]	[47]	[15]				[48]
Zn	[49]	+	[50]					[48]
Li	[51]							
Fe	[15]		[27]		[52]			
Co	[15]		[53]	[54]				
Ni	[55]	[15]	[56]				[56]	
Cu	[15]	[57]	[50]	[57]		[58]		
Mn	[54]							
Ca	[59]	[48]						
Cd	[22]							
Sn	[60]	[60]						

Note. The symbol "+" indicates that the information can be found in many sources.

The double hydroxides listed in Table 2 show anion exchange properties only at certain M^I/M^{II} ratios and with the condition that certain requirements are met in their synthesis. When these requirements are not met and at other ratios, the products may show not anion exchange but cation exchange properties, or may not be formed at all.

Table 3 lists double hydroxides with anion exchange properties, but these data were taken from the patent literature, and should be approached with care.

Double hyroxides with anion exchange properties are not formed for all M^I-M^{II} combinations. In particular, they are not formed if one of the ions M^{n+} oxidises the other M^{m+} (for example Fe^{3+}/Mn^{2+}). Moreover, although transition metals (Cr, Co, Ni, etc.) form double hydroxides, this is accompanied by the secondary formation of the oxides, hydroxides, and carbonates of the metals, and their mixtures. Solutions containing ions which can be readily oxidised in air must be treated in an inert atmosphere.

Table 3. Literature sources containing information on synthetic double hydroxides having anion exchange properties.

M^{II}	M^I								
	Al	Fe	Cr	Sc	Y	Ti	In	B	Bi
Mg	+	[47]	[61]	[61]	[61]	[61]	[62]	[62]	
Ni	[63]	[64]	[63]						
Zn	[63]	[64]	+			[62]	[62]	[62]	
Ca	[67]	[64]	[64]						
Ba	[68]	[64]	[64]						
Cu	[64]	[65]	[64]						
Co	[66]	[66]	[64]			[69]			
Fe	[64]	[64]	[64]						
Mn	[70]								
Al						[71]			
Cd	[62]	[62]	[62]				[62]	[62]	[62]

Note. The symbol "+" indicates that the information can be found in many sources.

The starting materials for preparing double hydroxides may be not only the salts but also the alkoxides of the corresponding metals, and the precipitation can be carried out by alkaline hydrolysis.[72] All the regularities described above should be observed in this case also, but by using the alkoxides of the appropriate alcohols an attempt can be made to produce the required structure in the process of synthesis.[73]

The mechanochemical method for obtaining double hydroxides appears more promising. Thus hydroxides based on zinc and chromium are obtained[42,46] either by grinding for 24 h at pH 4 a paste of zinc oxide and chromium salt (with an excess of the chromium salt) or by mechanically mixing dry zinc oxide and chromium(VI) oxide.[42] In the last case the mixture was moistened slowly with grinding, after which an equivalent quantity of water (16% of the total mass of the oxides) was added. The double hydroxides obtained by these methods had different properties; in particular, the specific surfaces of different specimens prepared by the "dry" method were 5, 13, and 22 $m^2 g^{-1}$, whereas those of specimens obtained by precipitating were 77 $m^2 g^{-1}$ and 99 $m^2 g^{-1}$. Coprecipitated hydroxides synthesised at different temperatures also have different specific surfaces (for hydrotalcite, 120 $m^2 g^{-1}$ at 65 °C and 12 $m^2 g^{-1}$ at 200 °C[35]).

The most promising method for obtaining complex hydroxides is by the sol–gel method, used to obtain hydrated salts.[28] Electrolytes are removed by decomposing the acid formed by passing an electric current. The decomposition gives sols of the corresponding hydrated oxides.

The most suitable initial salts are of course the chlorides, iodides, etc. The redox potentials of the metals may also influence the selectivity of the process, but by using different membranes—semi-permeable ion exchange membranes and porous crystalline membranes—it is possible to obtain various metal hydroxides. The sol–gel method has been used to obtain various sorbents based on metal hydroxides,[74–76] but there are no published data on the synthesis of complex basic hydroxides.

The alkali metals, except lithium form hydroxometallates or double basic salts with corresponding trivalent metals. Lithium also forms compounds with basic and anion exchange properties, but with a different structure. The lithium aluminium compound $[LiAl_2(OH)_6]OH$ has been studied in most detail.[24,30] Most workers tend to regard it not as product of the isomorphous replacement of some cations by others but as a product of the intercalation of lithium ions into the aluminium hydroxide lattice.[51] Lithium aluminium hydroxide can be obtained both by the traditional method of precipitation[77] and by solid-phase synthesis from crystalline $Al(OH)_3$ and lithium hydroxide[51] or the corresponding salts.[78] The yield is quantitative only when $Al(OH)_3$ particles are impregnated with LiOH. The optimum ratio of the liquid and solid phases is 5 : 1.[79] $Li_2Al_2(OH)_8$,[80] which also shows anion exchange properties, is less stable.

Theoretically, the exchange capacity of double hydroxides can reach high values—up to 5 mequiv g^{-1} for the hydroxides of light metals. A value of the anion exchange capacity of 3 mequiv g^{-1} (Mg, Al) has been given.[81] The real values differ considerably from the theoretical, however.

The factors responsible for the anion exchange or cation exchange properties of double hydroxides can be considered.

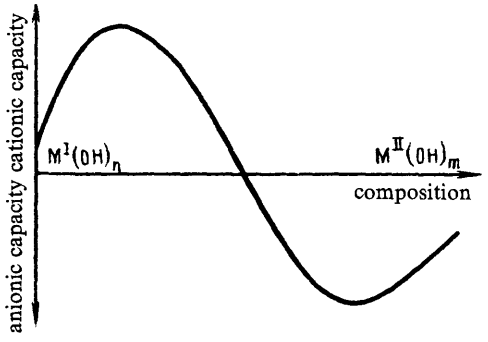


Figure 1. Composition dependence of the ion exchange capacity of a complex hydroxide.

If metal cations with charges lower than that on the original cations are introduced by isomorphous replacement into a polymeric hydroxide layer [for example if some Al^{3+} in $Al(OH)_3$ are replaced by Mg^{2+}], then the layer acquires an overall negative charge and begins to show cation exchange properties. If on the other hand cations with higher charges are introduced into the hydroxide layer [for example if some Mg^{2+} in $Mg(OH)_2$ are replaced by Al^{3+}], then the positively charged layer acquires anion exchange properties.

The ion exchange capacity should obviously depend on the degree of isomorphous replacement; a double hydroxide of metals in different oxidation states can be both a cation exchanger and an anion exchanger. The presence of ion exchange centres is determined by the displacement of electron density and the redistribution of charges.[82] There exists an optimum degree of isomorphous replacement, at which the maximum ion exchange capacity is reached.

Although lithium aluminium hydroxide is formed not by isomorphous replacement but by the introduction of Li^+ ions oetween two $Al(OH)_3$ layers, leading to the production of a positive charge,[77] all that has been said about the relationship between the isomorphous statistical replacement and the strength and number of basic and acidic centres remains applicable in this case also. The other alkali metal hydroxides show genuine isomorphous replacement.[83–86]

The approximate form of the composition dependence of the acid–base properties of a double hydroxide is shown in Fig. 1. The overall or observed exchange capacity is characterised, for example, by the pH of a salt solution when the ion exchanger is immersed in it; this pH is determined by the cation exchange and anion exchange reactions.

The dependence of the number of basic centres E on the surface of MgAl hydroxide in the carbonate form on the degree of replacement[87] is given as an example in Fig. 2.

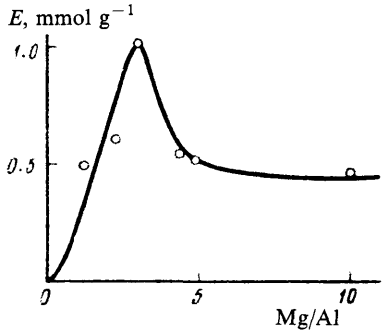
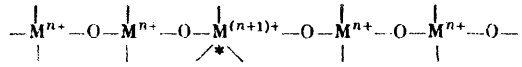


Figure 2. Composition dependence of the capacity of magnesium aluminium hydroxide.[87]

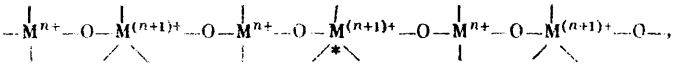
Similar observations were reported in another paper.[88] The curve shown in Fig. 1 was not obtained completely in any case, although the extremal character of the composition dependence of the capacity is mentioned in many papers. This curve naturally cannot be continuous, since the double hydroxide phases do not exist at all M^I/M^{II} ratios.[39] A study[29] of the formation of $Fe^{II}-Fe^{III}$ hydroxides gave the following results (the plus sign indicates that a double hydroxide is formed, the minus sign indicates that it is not formed, and i indicates impurity)

Fe^{II}/Fe^{III}	5.1	4.1	3.2	2.9	3.1	6.9	3.0	6.6	4.7	7.6
Hydroxide	+	+	+, i	–	+	+, i	+, i	–	–	–

The chief factors determining the number of basic centres (the exchange capacity) and their strength are the number of isomorphous replacements and their frequency. A centre of the type indicated by the asterisk



should obviously have a much higher basic strength than a centre of the type



because of the greater displacement of electron density. Account must of course be taken of the fact that the inductive influence decreases rapidly with increase in the distance, and becomes practically insignificant after two chain units.

What has been said about the relationship between the degree of isomorphous replacement and the strength and number of basic centres remains applicable when the oxidation states of the metals are equal, as for example in $Mg_xNi_{1-x}(OH)_2$.[89] In the examination of these systems it is necessary to compare the effective charges on the atoms; strictly speaking, this should also be done in all other cases.

The strength of the basic centres and the exchange capacity are inversely proportional to one another. The greatest strength should be shown by the basic centre in a specimen in which isomorphous replacement of one single atom has taken place; this specimen will have the lowest capacity. Correspondingly, the strength of the basic centres will be lowest in the specimen with the highest capacity.

The strength distribution of the basic centres can be predicted qualitatively by examining the structure of the specimen. Restricting the treatment to an idealised one-dimensional model, the following cases can be distinguished:

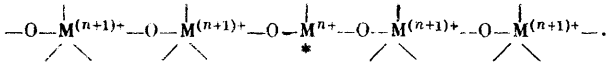
1) –A–A–A–A–B–A–A–A–A–
2) –A–A–A–B–A–A–B–A–A–B–A–A–A–
3) –A–A–A–B–A–B–A–B–A–A–A– .

Combinations of these are also possible. The inductive influence extending over more than three atoms can be neglected. The spectrum of the basic strength of real octahedral and tetrahedral systems in layer hydroxides is more complex, but the general approach remains the same.

For any ratio M^I/M^{II}, the real structure of layer hydroxides is far from ideal, that is from a regular alternation of isomorphous replacement centres ...AABAABAAB...

When the structures of double hydroxides is discussed, we refer to the isomorphous replacement of some cations by others. This treatment is extremely convenient, but it does not necessarily take place in practice. It is most likely, at any rate in hydrothermal synthesis, that the process taking place is not replacement but growth of the oxide chain, the sequence in which the cations are arranged in this chain being determined statistically, with allowance for their reactivity. Since the statistical factors are decisive, in real

complex hydroxides at all stoichiometric ratios, acidic centres of the following type exist



The number and strength of acidic centres undoubtedly also depend on the degree of isomorphous replacement.[90,91] A study[90] of the dependence of the number of basic and acidic centres on the degree of isomorphous replacement, that is on the ratio M^{I}/M^{II}, gave the following results:

Molar ratio MgO/Al_2O_3	2.49	3.8	5.23	9.33	17.6
Acidity, mmol g^{-1}	0.41	0.32	0.21	0.06	0
Basic strength, mmol g^{-1}	0.63	0.54	0.73	0.85	0.94 .

The basic centres were determined by titrating with a 0.1 M solution of benzoic acid in benzene in the presence of 2,4-dinitroaniline.

The strength of the basic centres lies mainly in the range $18.0 > H_0 > 17.2$. Thus the curve given in Fig. 1 is in fact the result of the summation of two curves giving the change in the number of basic and acidic centres (Fig. 3).

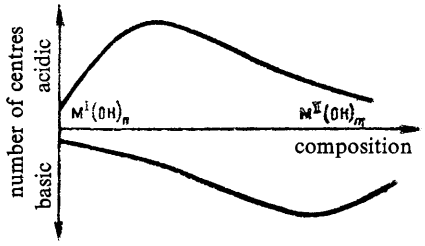


Figure 3. Dependence of the number of basic and acidic centres on the composition of double hydroxides.

Table 4. Observed and calculated exchange capacities of double magnesium aluminium hydroxide.

Capacity, mmol g^{-1}		Anion	References
theoretical	observed		
1.7	0.1	SO_4	[18]
1.6	1.0	SO_4	[74]
4.5	1.5	CO_3	[36]

The actual magnitude of the exchange capacity of double hydroxides differs considerably from the theoretical value calculated from elemental analysis data. There are two main reasons for this—inaccessibility of the centres and the presence of structural defects. The term structural defects is applied to the above-mentioned isomorphous replacements and breakdown of the sequence in the arrangement of the cations in the three-dimensional structures, shown in Fig. 4.

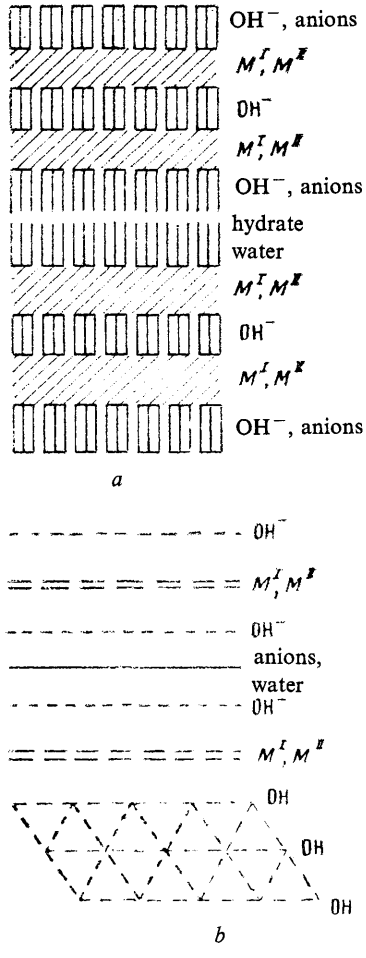


Figure 4. Diagram of the structure of a double hydroxide (*a*)[16] and the structure of hydrotalcite (*b*).[56]

The exchange capacity of a complex hydroxide cannot be regarded as the sum of the capacities of the individual hydroxides, as has been done.[52]

The exchange capacities of hydroxides of the $M^{I}_{x}M^{II}_{y}$ type also are not additive quantities, as indicated by the composition dependence of the anion exchange capacity of the double nickel magnesium hydroxide (Fig. 5).[92]

The observed exchange capacities are practically never equal to the theoretical values (Table 4).

Although the observed exchange capacity is much lower than the value calculated from the elemental analysis data, there is no reason to suppose that exchange involves only those centres on the outer

surface. This can be illustrated by the following example. Theoretically, the exchange capacity of ZnCr hydroxide in the carbonate form is about 1.6 mmol g^{-1}, but in practice the value is about 1.0 mmol g^{-1}; on the other hand, the specific surface of the specimen is about 150 $m^2 g^{-1}$, and the outer surface is about 3 $m^2 g^{-1}$.[45] If only the centres on the outer surface functioned, then the exchange capacity values should also differ by a factor of 50.

The internal centres in double hydroxides are accessible even to extremely complex organic molecules. The view is held that ion exchange taking place does not prove that the centres are accessible, and that the actual exchange may take place on the external surface after migration of ions from the internal space.[45] These suggestions, however, are not consistent with a large amount of data on the relationship between the size of the internal cavities and the size of the exchanging anions. The interplanar spacings in various double hydroxides are given in Table 5.

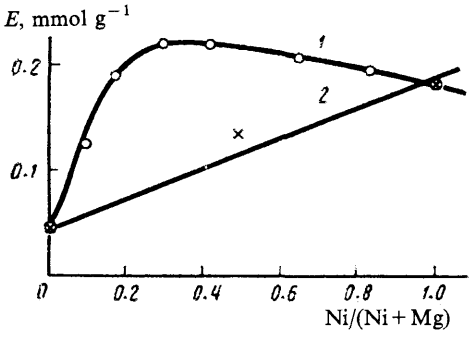


Figure 5. Dependence of the capacity of a hydroxide on its degree of isomorphous replacement:[92] *1*, complex NiMg hydroxide; *2*, mechanical mixture of Ni and Mg hydroxides.

The interplanar spacing is determined not only by the type of anion.[101] On ion exchange in which anions of one type are replaced by anions of another type, the change in the distance between the layers takes place abruptly,[44,56] and the appearance of phases with mixed anions in the space between the layers is unlikely, since this is energetically unfavourable because of the high activation energy of anion transfer. If nevertheless the hydroxide contains either alternating layers or separate regions with different anions within a given inter-layer space, which leads to deformation of the layers, then the determination of the interplanar spacings is complicated by the marked broadening of the X-ray diffraction lines.

The interplanar spacings also depend on the crystal structure of the complex hydroxide. This dependence is not so great, however; for example, the difference between the interplanar spacings for the hexagonal and trigonal forms of pyroaurite is 0.16 Å.[102]

The interplanar spacing is influenced much more strongly by the type of solvent in which anion exchange takes place and which acts as solvating agent. If water is used as solvent, there are usually 1–3 molecules of solvating water for every basic centre.

Table 5. Dependence of the interplanar spacings in double hydroxides on the nature of the anion.

Anion *	Interplanar spacing	References	Anion *	Interplanar spacing	References
Magnesium–aluminium			**Zinc–chromium**		
OH^-	7.55	[81]	C_2	4.6	[22]
F^-	7.66	[81]	C_3	5.0	[22]
Cl^-	7.87	[81]	C_4	6.0	[22]
Br^-	7.95	[81]	C_6	7.4	[22]
NO_3^-	8.79	[81]	C_{10}	8.4	[22]
I^-	8.16	[81]	Cl^-	7.7	[44]
CO_3^{2-}	7.65	[81]	I^-	8.3	[44]
NY	13.0	[81]	NO_3^-	9.1	[44]
SO_4^{2-}	8.58	[81]	ClO_4^-	11.9	[44]
$SiV_3W_9O_{40}^{7-}$	14.5	[93]	CH_3COO^-	12.9	[44]
$H_2W_{12}O_{40}^{6-}$	14.5	[93]	MoO_4^{2-}	10.45	[45]
$SiW_{11}O_{39}^{8-}$	14.5	[93]	F^-	7.51	[46]
$PW_9O_{34}^{9-}$	14.5	[93]	Cl^-	7.73	[46]
$Ru(DPS)_4^{4-}$	22.0	[94]	Br^-	7.85	[46]
$ReO_2(CN)_4^{3-}$	22.0	[95, 96]	I^-	8.4	[46]
Cl_4^-	22.0	[97]	N_3^-	7.62	[46]
CrO_4^{2-}	8.94	[23]	NO_3^-	8.88	[46]
$Fe(CN)_6^{3-}$	11.18	[98]	ClO_4^-	11.8	[46]
ClO_4^-	9.15	[98]	$^1/_2SO_4^{2-}$	11.8	[46]
CO_3^{2-}	7.7	[99]	$^1/_2HPO_4^{2-}$	10.9	[46]
Cl^-	7.7	[99]	AC_8	21.1	[46]
$HGaO_3^{2-}$	7.96	[99]	AC_{10}	23.7	[46]
MoO_4^{2-}	7.8	[99]	AC_{12}	26.1	[46]
SO_4^{2-}	8.6	[99]	AC_{14}	28.0	[46]
HPO_4^{2-}	8.29	[99]	AC_{16}	28.6	[46]
CrO_4^{2-}	8.73	[99]	AC_{18}	32.6	[46]
SiO_3^{2-}	8.74	[99]	**Nickel–iron**		
HVO_4^{2-}	9.33	[99]	CO_3^{2-}	7.97	[56]
Nickel–cobalt			Cl^-	7.86	[56]
CO_3^{2-}	7.66	[56]	NO_3^-	8.28	[56]
Cl^-	7.78	[56]	SO_4^{2-}	10.6	[56]
NO_3^-	8.53	[56]	ClO_4^-	11.94	[56]
SO_4^{2-}	11.19	[56]	CH_3COO^-	12.02	[56]
ClO_4^-	11.76	[56]	**Lithium–aluminium**		
CH_3COO^-	12.55	[56]	OH^-	7.5	[100]
			Cl^-	7.75	[100]
			HCO_3^-	7.6	[100]
			NO_3^-	8.8	[100]
			CH_3COO^-	13.0	[100]
			$^1/_2SO_4^{2-}$	8.7	[100]
			CO_3^{2-}	7.67	[100]

*Notation used: NY = Naphthol Yellow; anions of dicarboxylic acids: C_2 = oxalic, C_3 = malonic, C_4 = succinic, C_6 = adipic, C_{10} = sebacic; normal alkyl sulphates: AC_8 = octyl sulphate, AC_{10} = decyl sulphate, AC_{12} = dodecyl sulphate, AC_{14} = tetradecyl sulphate, AC_{16} = hexadecyl sulphate, AC_{18} = octadecyl sulphate; DPS = 4,7-diphenyl-1,10-phenanthroline disulphate.

Change in the degree of solvation leads to a change in the interplanar spacings,[103,104] and this may take place gradually or abruptly. Miyata and Okada[23] obtained two values for the interplanar spacing, depending on the moisture content of the specimen; no intermediate values were observed. Replacing water by another solvent with bulkier molecules leads to an increase in the interplanar spacing.

Table 6 shows the change in the interplanar spacings when a double zinc chromium hydroxide in the alkyl sulphate form is kept in different alcohols.

Table 6. Change in the interplanar spacing when a layer double hydroxide of zinc and chromium is kept in various normal alcohols.[46]

Alcohol	d, Å	Alcohol	d, Å
C_3H_7OH	28.3	$C_{10}H_{21}OH$	38.2
C_4H_9OH	29.2	$C_{12}H_{25}OH$	41.1
$C_6H_{13}OH$	30.8	$C_{14}H_{29}OH$	42.4
$C_8H_{17}OH$	33.7	$C_{16}H_{33}OH$	44.9

The influence of both the length of the hydrocarbon group in the anion and the length of the group in the solvent molecule on the interplanar spacing is given by the equation

$$d=a+bn,$$

where a and b are the contributions to the increase in the interplanar spacing made by the terminal (methyl and functional) groups and the CH_2 group respectively.[29] This relationship is possible for mutually perpendicular or almost mutually perpendicular arrangements of the hydrocarbon groups in the basal plane. In fact, it is known that the ions of dibasic acids can bind neighbouring hydroxide layers.[98,105] It is also known that after the ion-exchange replacement of the NO_3^- ion in zinc chromium hydroxide by alkyl sulphate anions and the alkylglycol sulphate anion $C_{12}H_{25}(OCH_2CH_2)SO_4^-$, the chains of the surface-active substances are arranged in a monomolecular layer strictly perpendicular to the layers of the hydroxide, and after drying the angle of slope is only 56°.[106] After drying, these heterolayer compounds retain the solvate molecules of the C_6-C_{18} alcohol solvents. A double layer consisting of alcohol molecules and the ions of the surface-active substance is formed.

Some workers assume that the interplanar spacing is determined not so much by the size of the counter-ions as by the structure and size of the anions present during the synthesis in the liquid phase. Thus when bulky alkyl sulphate anions are used in the synthesis, the interplanar spacing is increased by 2–3 Å, but when anion exchange involves lauryl sulfate, toluenesulphonate, dihydroxybenzene-sulphonate, terephthalate, or $Mo_7O_{24}^{6-}$, $W_7O_{24}^{6-}$, and $V_{10}O_{28}^{6-}$ anions, the interplanar spacing remains unchanged.[107]

The change in the interplanar spacing and exchange capacity of MgAl hydroxide during the sorption of various C_1-C_{20} primary and secondary alcohols has been studied.[108] A correlation was observed between the length of the group of the alkyl alcohol and the exchange capacity of the anion exchanger, and it was shown that the active centres are blocked by the hydrocarbon groups. At the same time, the absence of any significant change in the interplanar spacing indicated parallel arrangement of the planes.

The interplanar spacing depends significantly on the degree of isomorphous replacement. This can be seen for the double hydroxide of magnesium and aluminium:[24]

Mole fraction Mg	0.09	0.69	0.71	0.73	0.95
d, Å	7.55	7.60	7.64	7.7	7.8

Thus the interplanar spacing is influenced by different factors. In certain cases, one or two of these factors are decisive (for example, the interplanar spacings in various double hydroxides of the types Zn_2Al, Zn_2Cr, and Ni_3Al containing the $V_{10}O_{28}^{6-}$ ion have the same value, 11.9 Å [109]), and in other cases the different factors have comparable effects.

Thermal treatment of the hydroxides leads to appreciable changes in their structure and composition and hence in their physico-chemical properties. These changes are naturally greatest when the thermal treatment is carried out in air or in another gaseous medium. In the liquid phase the changes are slight. Thus MgAl and ZnCr hydroxides undergo no changes when heated to 150–170 °C in an aqueous or alcohol medium.[143]

In the thermal treatment of hydroxides in a gaseous medium, two main processes take place—the loss of solvating water and dehydration with breakdown of the brucite-like layer. Typical thermal analysis curves are shown in Fig. 6. The first endothermic effect, corresponding to the loss of the solvating water and breakdown of the carbonium ion [sic. carbonate ion? Ed. of Translation)], is observed in the range 200–250 °C, and the second, corresponding to dehydration is observed at 400–450 °C. The position of the peaks depends on the molar ratio of the cations and on the nature of the anion.

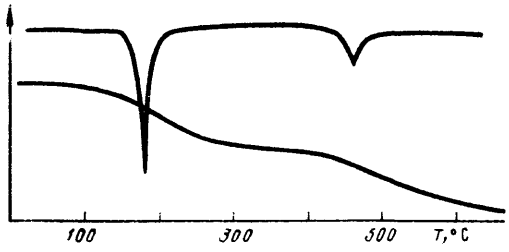


Figure 6. Typical thermal analysis curves for a double hydroxide.[55]

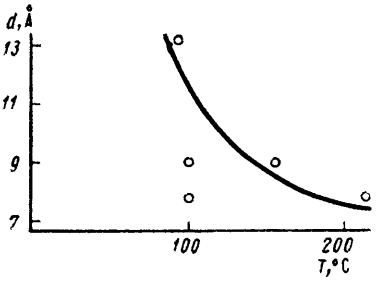


Figure 7. Dependence of the interplanar spacing in lithium aluminium hydroxide on the temperature at which dehydration starts.[100]

The temperature at which the first endothermic effect appears for lithium aluminium hydroxide (°C) has the following values for different anions:[110] CO_3^{2-} 120, SO_4^{2-} 130, OH^- 139, NO_3^- 201, Cl^- 250.

At the same time, the dependence of the interplanar spacing in this hydroxide on the temperature at which dehydration starts has the form shown in Fig. 7.

For the thermal treatment of MgAl hydroxide,[111] completely different values were obtained for the temperature at which dehydration starts, °C: OH^- 165, CO_3^{2-} 200, SO_4^{2-} 200, Cl^- 240, NO_3^- 140.

The strength of the retention of water in the space between the layers is most probably determiend by the strength of the hydrogen bond, with allowance for the mutual repulsion of the anions.

In general, the greater the bond strength, the higher the temperature at which water is removed. The first endothermic process involving the loss of water of crystallisation is completely reversible; when the product obtained by heating is placed in water, all its physicochemical properties are restored. Breakdown of the brucite-like layer on dehydration leads to the production of spinel-like structures. Contrary views that this process is completely irreversible[90] and that it is completely reversible[99] have been expressed.

A study of the behaviour of MgAl hydroxide when treated with water after heating at 600 °C showed[108] that the original hydroxide, with the same anion exchange properties is restored.

The structure and properties of MgAl oxide obtained by heating the corresponding hydroxide have been studied.[99] Specimens heated at 900 °C sorbed water from the gas phase, with complete restoration of the original hydroxide structure. An interesting feature is that the properties and structure of the restored hydroxide depended on the type of anion in the solution, although its concentration did not exceed 0.05%.

The reversibility of the processes taking place on thermal treatment is confirmed indirectly by the fact that the double hydroxides can be obtained by hydrolysing the corresponding oxides.[112]

Thermal treatment generally decreases the interplanar spacings, as a result of a rearrangement and a decrease in the width of the internal layers.

The temperature dependence of the interplanar spacing in Mg-Al hydroxide is shown below.[98]

T, °C	20	100	150	200	250
d, Å	11.18	10.91	10.39	10.80	8.04

In the gas phase the distance between the layers is determined not only by the type of anion but also by the degree of hydration, which in turn depends on the partial pressure of water vapour.[59,100]

The thermal treatment of double hydroxides influences their sieve properties, and also the number and strength of the basic centres. The dependence of the number of basic centres on the treatment temperature is generally extremal in character.

The highest number of basic centres is produced in MgAl oxide obtained by heating the hydroxide at 450 °C; the basic strength of specimens heated below 400 °C is too low.[113]

The indicator method has been used to determine separately the change in the numbers of Brönsted and Lewis basic centres when ZnCr hydroxide is heated in air (Fig. 8).[108]

There are insufficient published data on the change in the strength of the basic centres on thermal treatment, and the solution of this problem lies in the future. Published data[87] show that the dependence of the strength of the basic centres on the treatment temperature is complex. At higher temperatures, thermal treatment of double hydroxides gives spinel structures,[43] and the temperatures of their formation are lower than those when a mixture of the hydroxides is heated.[114]

Thermal treatment at high temperatures leads to the appearance of acidic centres. The formation of acidic centres when Zn-Cr hydroxide was heated was observed only above 500 °C (the number of centres was less tha 0.1 mmol g^{-1-1}).[108] The change in the number of acidic centres when double Mg-Al hydroxide is heated is shown in Fig. 9.

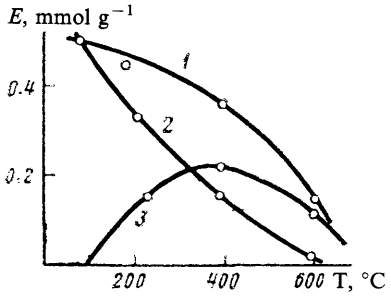


Figure 8. Change in the number of basic centres when zinc chromium hydroxide is heated in air:[108] *1*, total; *2*, Brönsted; *3*, Lewis.

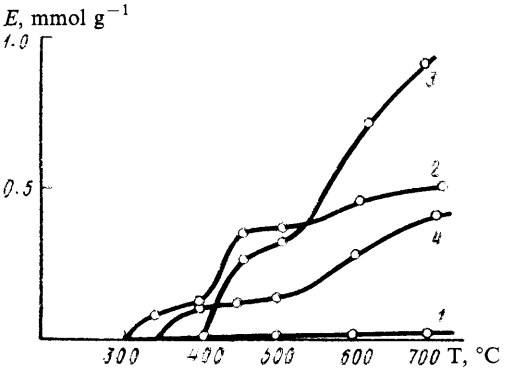


Figure 9. Change in the number of acidic centres when double magnesium aluminium hydroxide is heated in air; Mg/Al molar ratio: *1*, 0.05; *2*, 4; *3*, 6; *4*, 10.[87]

The specific surface of complex hydroxides can vary over a wide range, but there are no definite data on which parameters determine this quantity. The dependence of the internal surface of the pores on the average pore radius has been given.[115] The specific surface is influenced by the crystallisation temperature (in the hydrothermal synthesis[35]). Thus crystallisation at 65 °C for 18 h gives platelets with dimensions of 0.5 μm and a surface are of 120 $m^2 g^{-1}$, whereas crystallisation at 200 °C for 18 h gives crystals with dimensions of 1–2 μm and a surface area of about 12 $m^2 g^{-1}$.

The external specific surface of double hydroxides obtained under industrial conditions has been measured by the diffraction of laser beams in suspensions of the hydroxide in water and in glycol solution. All the hydroxides were obtained by precipitating from concentrated solutions at low temperatures. Different double hydroxides had the following surface areas, $cm^2 g^{-1}$: Mg-Al 674, Zn-Cr 298. When Zn-Cr hydroxide was kept for a long time in aqueous methanol, its specific surface increased to 592 $cm^2 g^{-1}$.[116] This is of course much smaller than hundreds of square metres per gram,[15,35] so that when the specific surface is mentioned, it must always be made clear whether the total surface or only the external surface is meant.

The surface area of hydroxides changes on thermal treatment, the changes being very different for different compounds, and also for the same compound obtained in different ways.[34,42] In most cases, thermal treatment leads to an increase in the specific surface. This is most probably due to the formation of a large number of fine pores (there is a two-fold increase in the surface area and the volume),[115] possibly as a result of the conversion of an appreciable proportion of the specimen from the octahedral to the tetrahedral state. Contrary data indicating a marked decrease in the specific surface on thermal treatment have also been published.[117]

In the liquid phase, double hydroxides have an extremely high thermal stability. They are very stable in basic media, but even in neutral media their stability is extremely high.[118] All double hydroxides undergo changes, however, in acidic solutions. The reaction with acids, as far as complete solution of the mineral framework, limits the possible applications of double hydroxides in acidic media.

Table 7. Anion exchange properties of various double hydroxides.

Anion exhanger	Selectivity series	References
Mg-Al	$I^- < Br^- < Cl^- < F^- < SO_4^{2-} \leqslant OH^- < CO_3^{2-}$	[81]
Li-Al	$AcO^- < CO_3^{2-} \approx NO_3^- < Cl^- < SO_4^{2-}$	[75]
Ca-Al	$AcO^- < NO_3^- < Cl^- < CO_3^{2-} \approx SO_4^{2-}$	[59]
Fe-Zr	$I^- < Br^- < Cl^- < MoO_4^{2-} \approx PO_4^{3-} < SO_4^{2-}$	[52]
Ni-Fe Ni-Co	$AcO^- < NO_3^- < ClO_4^- < Cl^- < SO_4^{2-} \ll CO_3^{2-}$	[56]
Zn-Cr	$AcO^- < ClO_4^- < MnO_4^- < NO_3^- < Cl^- < CO_3^{2-}$	[44]

The stability of hydroxides in basic and neutral media depends on many factors, however.[119] In solution, for example, calcium aluminium hydroxide sulphate reacts with carbon dioxide in the pH range 9–12 and is converted completely into the corresponding carbonates and hydrogen carbonates.[114] The same reaction takes place between CO_2 and the dry hydroxide sulphate, Zinc chromium basic nitrate is also fairly unstable in neutral solutions; it is hydrolysed to give the individual basic salts, or zinc oxide if the process is prolonged sufficiently.[24] This question was examined in more detail in a study[40] of double hydroxides of chromium and nickel to determine how and why their sorptive capacity changed. No definite correlation was found between the concentration of hydroxide groups and the exchange capacity (the capacity gradually decreases, and the concentration of hydroxide groups and structural water increases slightly).

Published data[39] would seem to indicate that the structure of double chromium zinc hydroxide is completely unstable. For example, at 20–60 °C and pH 6.5–7.0 the hydroxide is hydrolysed rapidly to zinc oxide and the basic nitrate. In fact, however, double zinc chromium hydroxide can exist for an extremely long time, and the exchange capacity of the corresponding nickel chromium hydroxide decreases by only about 15% after 6 months.[40] Double hydroxides can be kept for an unlimited time at high pH values.[33,120]

The effective exchange capacity also depends on the pH of the solution, the effect being greatest for amorphous compounds.[121] The stronger the basic properties of a compound, the weaker the influence of the pH of the medium on the exchange capacity.

Ion exchange in double hydroxides has been studied in considerable detail. The selectivity series for ion exchange by various hydroxides are given in Table 7.

The selectivity series given in various other sources are less complete than those in Table 7. Deviations from these sequences are observed.

The selectivity series given correspond almost completely to the magnitude of the interplanar spacings (see Table 5) and hence to the sizes of the ions, although in general the selectivity of inorganic anion exchangers depends on the characteristics of the synthesis.[122,123] The interplanar spacings in double hydroxides, unlike those in ion exchange resins, correlate with the sizes of the non-hydrated ions. The CO_3^{2-} ion shows the highest stability to exchange, probably because of the planar arrangement of the oxygen atoms and the high effective ionic charge.

Since practically all double hydroxides show a high selectivity with respect to carbonate ions, the preparation of double hydroxides as the pure sulphates, chlorides, etc. by ordinary ion exchange is not always possible, although theoretically there are no problems.[81] A much more effective method has been proposed.[124] MgAl and NiAl hydroxides in dilute acid solutions lose carbon dioxide rapidly and completely as a result of the exchange

$$DH.CO_3 + 2HCl \rightarrow DH.Cl_2 + CO_2 + H_2O.$$

This reaction can take place with any acid stronger than carbonic acid.[125]

Anion exchange in double hydroxides takes place not only with ordinary inorganic anions but also with the anions of dicarboxylic acids,[22] anionic complexes,[21,52,99] complex alkyl sulphates and alkanesulphonates,[46,126] optically active compounds,[127] alkyl halides,[45,128] and hydroxyalkylated alcohols.[162]

Double hydroxides are anion exchangers not only in liquid media but also in gaseous media.[45]

The rate of ion exchange in a liquid phase depends markedly on the pH of the medium. Anion exchange by NiFe hydroxide at pH 0–3 takes not more than a few minutes, whereas at pH > 6 no exchange has taken place after several hours. The $Cl^- \rightleftharpoons OH^-$ exchange rate constants in NiAl hydroxide in neutral and basic media are 1.4×10^3 s^{-1} and 9×10^3 s^{-1} respectively.[129] The types of cation present in the solution have a marked influence on the rate of exchange.[21]

V. Natural double hydroxides

Inorganic anion exchangers belonging to the class of complex hydroxides can be synthesised, and also occur naturally as various minerals. Almost all these minerals belong to the pyroaurite–sjögrenite group, since their elementary structure corresponds fairly closely to the general formula of pyroaurite (trigonal form) or sjögrenite (hexagonal form).

Table 8 lists minerals of this group and corresponding minerals having anion exchange properties. This Table can be reduced considerably if account is taken of the fact that all the minerals listed in it are capable of ion exchange. The name can be based on the hydroxide form of the mineral, correpsonding to the traditional nomenclature of ion exchange resins: "meixnerite carbonate" or "meixnerite in the carbonate form" instead of "hydrotalcite". Alternative names can be formed in accordance with accepted mineralogical nomenclature, taking as a basis the most stable natural form, that is the carbonate form. It is then necessary to use the name "hydroxohydrotalcite" instead of "meixnerite", and "sulphotakovite" instead of "carrboydite".

Table 8. Natural anion exchange minerals.

Name	Formula	Symmetry	Impurities	References
Hydrotalcite (Faulknerite)	$Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$	trigonal	Ni, Cl	[102, 130]
Manasseite	$Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$	hexagonal		[102]
Stichtite	$Mg_6Cr_2(OH)_{16}CO_3\cdot 4H_2O$	trigonal	Fe	[102, 130]
Barbertonite	$Mg_6Cr_2(OH)_{16}CO_3\cdot 4H_2O$	hexagonal		[102]
Pyroaurite (Igel'stremit)*	$Mg_6Fe_2(OH)_{16}CO_3\cdot 4H_2O$	trigonal	Fe, Al, Ni	[102]
Sjögrenite	$Mg_6Fe_2(OH)_{16}CO_3\cdot 4H_2O$	hexagonal		[102]
Brugnatellite	$Mg_6Fe(OH)_{13}CO_3\cdot 4H_2O$	trigonal		[102, 130]
Kolingit*	$Mg_{10}Fe_2(OH)_{24}CO_3\cdot 2H_2O$	hexagonal		[102, 130]
Cyanotrichite	$Cu_4Al_2(OH)_{12}SO_4\cdot 2H_2O$	–		[130]
Woodwardite	$Cu_4Al_2(OH)_{12}SO_4\cdot(2\div 4)H_2O$			[124, 130]
Meixnerite	$Mg_3Al(OH)_9\cdot 2H_2O$	trigonal		[131]
Motukoreaite	$Mg_{10}Al_6(OH)_{28}(CO_3)_3\cdot(SO_4)_2\cdot 14H_2O$	hexagonal		[130]
Takovite	$Ni_6Al_2(OH)_{16}CO_3\cdot 4H_2O$	trigonal		[124, 132]
Reevesite	$Ni_6Fe_2(OH)_{16}CO_3\cdot 4H_2O$	"		[133]
Carrboydite	$Ni_3Al_2(OH)_{10}SO_4\cdot H_2O$	hexagonal		[134, 135]
Aiovatit*	$Mg_4Fe(OH)_{16}Cl\cdot H_2O$	"		[124]
Hydrocalumite	$CaAl_2(OH)_6OH\cdot 6H_2O$	–	$\frac{1}{2}SO_4$	[124]
Khonessit*	$Ni_6Fe_2(OH)_{16}SO_4\cdot 4H_2O$	–		[124]
Comblainite	$Ni_6Co_3(OH)_{18}(CO_2)_2\cdot 9H_2O$	orthorhombic		[136]
Erdlegit*	$Zn_6Al_2(OH)_{16}CO_3\cdot 4H_2O$	–		[137]
Ettringite	$Co_6Al_2(OH)_{16}(SO_4)_3\cdot 26H_2O$	–		[33]
Aurichalcite	$Cu_2Zn_3(OH)_6(CO_3)_2$	–		[138]

[*Transliterations. Equivalents in Western nomenclature are not clear. (Ed. of Translation)].

It would be quite incorrect to use names such as, for example, "chromobrugnatellite"[102] instead of "stichtite", since when M^I or M^{II} is replaced the structure and properties of the mineral may be changed considerably.

Of the minerals having anion exchange properties, only hydrotalcite is widely encountered, and all the others are relatively rare or very rare minerals.

Like the other minerals, the compounds showing anion exchange properties have been studied mainly from the mineralogical viewpoint, that is most attention has been paid to their structure and chemical composition.

For an understanding of the characteristics of ion exchange and an evaluation of the minerals as possible anion exchangers, most information is given by the following mineralogical data: chemical composition, interplanar spacing, stability in aqueous solutions, thermal analysis data, and data on the isomorphous replacement of cations and anions.

The chemical compositions of the minerals have been determined fairly accurately, and the data obtained by different authors show no discrepancies. Sometimes, minerals with complex compositions are encountered, for example $Mg_3Zn_3Al_2(OH)_{16}CO_3$, or isomorphously substituted minerals in a background of the basic mineral, for example ferristichtite in mixtures or intergrowths with stichtite.[130] The isomorphism is often determined by the rock in which the given mineral occurs.

The interplanar spacings depend mainly on the anion. Replacement of the anion has a much greater effect on the interplanar spacing than the isomorphous replacement of a cation. The interplanar spacing changes little in the series hydrotalcite (Mg, Al)–stichtite (Mg, Cr)–pyroaurite (Mg, Fe), the values being 7.83, 7.8, and 7.6 Å respectively.[102,130] Anion exchange leads to a greater change in the interplanar spacing: 7.64 Å for meixnerite (Mg, Al, OH), 7.83 Å for hydrotalcite (Mg,Al,CO_3), and 11.32 Å for motukoreaite (Mg,Al,SO_4).[102,130]

The polymorphic form has comparatively little influence on the interplanar spacing. The interplanar spacings for different minerals are (Å): pyroaurite (trigonal form) 7.6, sjögrenite (hexagonal) 7.78; and hydrotalcite (trigonal) 7.83, manasseite (hexagonal) 7.67.[130]

The interplanar spacings in minerals are influenced not only by the nature of the anion but also by the solvated state of the ion being exchanged. Anionic minerals can sorb both solvated and non-solvated anions. The transfer of solvating water from the solid to the gas phase and back takes place readily even at room temperature, the direction of the process depending on the humidity of the surrounding medium. For example, carrboydite loses water reversibly, as a result of which the interplanar spacing decreases from 10.5 Å to 8.6 Å.[134] When the humidity of the medium changes from 0 to 100%, only two values of the interplanar spacing are observed in takovite—10.8 Å at a high humidity and 8.9 Å at a low humidity.[124] The same phenomenon is observed for motukoreaite (11.1 Å at a high humidity and 8.7 Å at a low humidity).[132]

If however the solvating agent is not water, the increase in the interplanar spacing may be even greater. Thus after hydrotalcite is treated with ethylene glycol,[124] the interplanar spacing is at first 12.9 Å, after which it gradually changes to 10.0 Å; when water is removed by drying, the spacing decreases to 7.87 Å. An additional ethylene glycol layer is apparently first produced in hydrotalcite, after which ethylene glycol solvates the exchange centres with the anions present there together with hydrate water, and finally ethylene glycol remains only as the solvating agent.

Diagnostic tests on minerals invariably include the action of various acids. In the study of practically all the minerals, breakdown of their structure and complete solution under the influence of strong mineral acids was observed; solution is generally accompanied by slight "effervescence".[98] Published data on the effect of aqueous solutions of mineral and organic acids are somewhat contradictory. Thus it has been reported[98] that brugnatellite dissolves readily in dilute acid solutions in the cold, and also[132,139] that treating pyroaurite minerals with dilute solutions of various acids does not lead to breakdown of the basic structure. The action of 0.1 M solutions of nitric, sulphuric, and hydrochloric acids on takovite and hydrotalcite has been studied.[124] X-Ray diffraction and infrared spectroscopy established that specimens treated with HCl and HNO_3 are identical to the untreated materials, except that they are in a different salt form. The diffraction patterns of the sulphate materials differ from those of the starting materials; the interplanar spacings increase as a result of the geometric differences between the leaving carbonate ion and the sulphate ion.

The stability of the anionic minerals in solutions of salts and bases has not been reported, but if the minerals are analogous to the synthetic layer double hydroxides, they should be extremely stable in these solutions.[33]

Thermal studies have been carried out only for the anionic minerals containing the carbonate ion.[130] Practically all of them give differential thermal analysis curves of identical form. Two endothermic effects are observed, the first in the temperature range 180–250 °C (300 °C for manasseite) due to the liberation of water of crystallisation, and the second in the range 420–500 °C (320 °C for kolingit) due to the loss of hydroxide water and carbon dioxide. Spinel formation takes place at higher temperatures.

The first process is completely reversible; keeping the heated specimen in a moist atmosphere restores the original structure. The second process, however, involving the loss of water and carbon dioxide, is irreversible, although restoration of the structure in a solution saturated with CO_2 has been reported.[131]

The non-carbonate forms of the anionic minerals have not been studied by thermal analysis, but the form of the DTA curves should be the same in this case also, apart from the appearance of additional peaks corresponding to the decomposition and removal of the anions.

Of much greater interest is the fact that although different anions are encountered in the minerals being considered, the structure of a mineral, usually determined by X-ray diffraction, remains unchanged. This indicates again the possibility of replacing the anions in the minerals, that is their anion exchange properties.

The anion exchange properties of the layer minerals have been studied only for takovite and hydrotalcites.[124] Their selectivity with respect to anions changes in the same order:

$$CO_3^{2-} > NO_3^- > OH^- > Cl^- > SO_4^{2-}.$$

The position of the sulphate ion in this series is unexpected. The existence of such minerals as cyanotrichite, woodwardite, and others encountered in nature in the sulphate form indicates stability of the sulphate forms. Carrboydite is found in weathered rocks, and if its selectivity with respect to the carbonate ion were a maximum, it should have been converted completely into takovite after a geologically momentary time interval. The work cited[124] in fact points out that the carbonate groups of the original mineral are readily exchanged for sulphate ions at room temperature. For the synthetic analogues, the following order of selectivity has been given:[81]

$$CO_3^{2-} > SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-.$$

VI. Inverse zeolites

The most promising anion exchangers are undoubtedly the inverse zeolites, which represent a completely new class of solids having basic properties; they were first described in 1987.[140]

Inverse zeolites, like other inorganic anion exchangers, are products of isomorphous replacement. In contrast to mixed hydroxides, salts, etc., however, in inverse zeolites it is not the metal ions that are replaced, but silicon ions, which are replaced by phosphorus ions. The introduction of an ion with a higher oxidation state produces an excess of positive charge, whose compensation requires anions.

The replacement of silicon by phosphorus in zeolites presents no problems. Inverse zeolites of the types NaX, NaA, KY, and 4A have been prepared and studied. Inverse zeoliites can apparently be obtained from zeolites of any type, and in general from any aluminosilicates. An important feature is that inverse zeolites retain practically completely the structure of the cavities of the original materials, although they do not contain the same quantity of water.

Inverse zeolites, like other anion exchangers obtained by isomorphous replacement, show the dependence of the strength and number of the basic centres on the degree of isomorphous replacement described above.

The exchange capacity of various inverse zeolites that have been studied[140] is 2–3 mequiv g^{-1}. Unfortunately, the composition dependence of the exchange capacity was not examined; it was merely reported that in the range of molar ratios P/Si from 0.002 to 0.05 there is no correlation between the exchange capacity and the phosphorus concentration. This result is somewhat unexpected, since if static isomorphous replacement is assumed, the number of centres should be practically linearly dependent on the concentration of the element introduced.

The concentration of phosphorus in inverse zeolites based on NaA,for treatment times of 17, 22, and 23 h, had the values 2, 4, and 50 mg g^{-1} respectively.[140] In a study by the present author, the anion exchange capacity of the same zeolite for treatment times of 9, 15, and 21 h had the values 0.56, 0.8, and 0.52 mequiv g^{-1} respectively; the concentration of acidic centres remained at practically the same level. The number of Brönsted basic centres was greater than the number of Brönsted acidic centres (more accurately, not the number but the sum of the products of the number of centres and their dissociation constant, $\Sigma k_i C_i$). The rate of ion exchange was not very high, since the contact time for its study was not less than one week. The selectivity of inverse zeolites with respect to the anions F^-, Cl^-, and NO_3^- is different; the isotherms of the $F-NO_3$ and $Cl-NO_3$ exchange processes have a sigmoid form. The selectivity of inverse zeolites with respect to carbonate ions is particularly high.

The thermal stability of inverse zeolites is determined practically by the properties of the starting material, so that they have a high thermal stability. The temperature at which the main dehydration begins for all the compounds studied is not lower than 400 °C. Their chemical stability is also similar to that of the original zeolites.

VII. Mercarbide

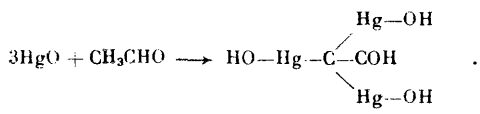
Salts of mercarbide, or simply mercarbides, are unique basic compounds. They have a high concentration of basic centres, a unique stability, and a well developed three-dimensional structure.

Salts of mercarbide are readily obtained by heating the yellow form of mercuric oxide for a long time in a highly concentrated solution of alkali in alcohol.[142] Red mercuric oxide can also be used, but the reaction rate is then lower. The rate is even lower if potassium or sodium alkoxides are used instead of the corresponding hydroxides.

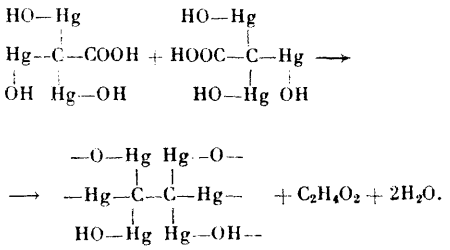
The initial stage of the process is possibly the oxidation of ethanol to acetaldehyde:

$$HgO+C_2H_5OH\rightarrow CH_3CHO+Hg+H_2O.$$

This is confirmed by the fact that an appreciable quantity of the original mercuric oxide is reduced to metallic mercury; the reaction is much more difficult in the absence of alcohol. The acetaldehyde formed is mercurated by three molecules of the oxide:



This compound is then oxidised by another molecule of mercuric oxide to give the sodium salt of the corresponding acid. Up to 40% of the original oxide is reduced to metallic mercury. Intermolecular removal of water gives mercarbide (water is also removed from the hydroxide groups of mercury):



In addition to ethanol as starting material it is possible to use saturated alcohols, aldehydes, cellulose, starch, and acids. Ethanehexamercarbide (the correctness of this name will be discussed below) can be obtained from ethanol and primary and secondary propanol. If the starting materials used are compounds which are not alcohols, or are alcohols whose molecular weight differs greatly from that of ethanol, the properties of the mercarbides obtained are quite different. Neither methanol nor formaldehyde give mercarbides or analogous products.

From the formula $C_2Hg_6O_2X_2$, where X is the exchangeable anion,

$$C_2Hg_6O_2X_2+2Y^-\rightleftharpoons C_2Hg_6O_2Y_2+2X^-,$$

the theoretical exchange capacity is about 1.5 mequiv g^{-1}. The actual values of the exchange capacity are extremely close to the theoretical value: 1.4 for the bromide ion, 1.5 for the hydroxide ion, and 1.5 for the chloride ion;[6] or 1.34 for the iodide ion, 1.37 for the ethoxide ion, and 0.052 for the chloride ion[143] (values in mequiv g^{-1}). The low value of the exchange capacity with respect to chloride ion in the last case is evidently due to the higher strength of the bond formed with the hydroxide ion compared with that with the chloride ion. Since the theoretical and actual values of the exchange capacity of mercarbides are approximately equal, the centres on the mercarbide surface and the centre in its bulk are evidently both accessible.

In some cases the exchange capacity of mercarbide can be increased considerably by carrying out the reaction

$$[C_2Hg_6O_2](OH)_2 \xrightarrow{HCl} [C_2Hg_6O_2]Cl_2 \xrightarrow{HCl} C_2Hg_6Cl_6.$$

This reaction is reversible, and treating the chloride with sodium hydroxide gives the original mercarbide. In this case, however, the structure undergoes significant changes.

The structure of ethanehexamercarbide, also called Hofmann's base in honour of the man who first studied it, indicates that it has active centres of only one type, namely Brönsted centres. The exchange capacity of mercarbide, established in a study of the basic centres by the indicator method in the presence of 2,4-dinitroaniline with pK_a = 15.0, was 1.5 mmol g^{-1}.[144] The same value was obtained when the exchange capacity was determined in KI and HI solutions. In the presence of 4-chloroaniline, however, the concentration of basic centres was 0.8 mmol g^{-1}. This may indicate that the mercarbide molecule contains centres of two types.

There is lack of agreement on whether mercarbides are derivatives of ethane[144,145] or methane.[146–149] The detection of centres of two types with different strengths in approximately equal quantities apparently indicates that the name "ethanehexamercarbide" is correct.[144] Further evidence that this compound is a derivative of ethane is provided by the fact that an exchange capacity higher than 1.5 mmol g^{-1}, that is higher than the theoretical value for ethanehexamercarbide, has never been observed, whereas the theoretical exchange capacity of methanetetramercarbide is 2.3 mmol g^{-1}.

A striking feature is that in all cases the elemental analysis data confirm the structure proposed by the authors concerned, although the same method was used to obtain the mercarbide.

Mercarbides have a rigid structure, and contain fairly large cavities, accessible to ions such as Br^-, I^-, SCN^-, ClO_4^-, SO_4^{2-}, and CrO_4^{2-}. C_7-C_{10} normal alcohols and benzoic acid can penetrate into the pores of mercarbide.[143]

The unique chemical stabilty of mercarbides is due to the strength of the C—Hg bond. The stability of mercarbide in acid solutions is particularly striking. Hydroxomercarbide reacts with acids to give the corresponding salts, which are stable in concentrated mineral acids, even aqua regia. It is also stable to oxidising agents such as potassium permanganate, chromic acid, hypochlorites, and hypobromites, but reacts slowly with reducing agents when heated (when heated with hydrazine hydrate it gives a mixture of gases, one of which is ethane[142]).

Treating mercarbide with acids gives salts of two types—the product of the replacement of two hydroxide groups and the product of the replacement of all the oxygen groups. There arises the question of how to characterise this property of mercarbides in terms of the basic properties and the ion exchange properties. On the one hand, the solid may sorb anions from the liquid (and gas) phase by a reversible process, that is apparently ion exchange. On the other hand, this basic or exchange centre cannot be determined *a priori*, either by the indicator method or by anion exchange. Hexaequivalent exchange can be detected only by titrating with highly

concentrated mineral acid, which leads to an unacceptable change in the structure.

The thermal stability of mercarbide is not as high as its chemical stability. When heated in air, hydroxomercarbide explodes with the effect of a high explosive; the published temperatures of the explosion vary from 120 °C [145] to 250 °C.[142] Our DTA studies showed that in air, mercarbide explodes at 140 °C, but in a liquid phase it is stable for an indefinite period at 200 °C.[143]

The order of selectivity of mercarbide with respect to various anions is as follows:[6]

$$NO_3^- < Cl^- < Br^- < OH^- \leqslant CN^- < I^-.$$

VIII. Heteropolar salts

Insoluble salts can often act as ion exchangers.[75] Their properties have been studied in detail.[6] All the compounds that have been described, however, are either cation exchangers or amphoteric substances. Only a few compounds based on salts and showing clearly defined basic properties over a wide range are known. One group of compounds of this kind is formed by transition metal tellurides.[150,151]

As noted above, it is difficult to draw a boundary between hydroxides and complex oxides obtained by heating hydroxides. A criterion is apparently provided by the conversion of the oxides into the hydroxides in an aqueous phase, observed, for example, for spinels obtained from mixed hydroxides, but not for the above-mentioned tellurides.

The tellurides of zirconium[150] and tin,[151] and also various molybdates,[152] are good anion exchangers with an extremely small number of acidic centres. The tellurides are obtained by hydrothermal synthesis in a strongly acidic medium. The precipitate is usually aged for a long time at increased temperature.

The anion exchange capacity of tellurides has been determined with respect to chloride ions, but it was subsequently established that these compounds show a low selectivity with respect to these anions. Tin telluride has a capacity of 1.12 mequiv g^{-1}, and zirconium telluride a capacity of 0.98 mequiv g^{-1}.[150,151]

The ideas about the statistical formation of exchange centres are also applicable to complex oxides and salts, but the deviations from the ideal distribution are much smaller in this case.

Tellurides are true ion exchangers, and anion exchange in these materials is completely reversible. For zirconium telluride, the selectivity decreases in the following anion order:[150]

$$CrO_4^{2-} \gg MoO_4^{2-} > SO_4^{2-} > PO_4^{3-} > AsO_4^{3-} > Fe(CN)_6^{4-} > Br^- > Cl^-.$$

For tin telluride the order is:[151]

$$SO_4^{2-} > PO_4^{3-} > Fe(CN)_6^{4-} > MoO_4^{2-} > CrO_4^{2-} > AsO_4^{3-} > SCN^- > NO_3^- > Cl^- > Br^-.$$

The tellurides are white solid amorphous substances, and their structure should be fairly rigid. They have a high chemical stability, and are stable for an indefinite period in acid (1–5 M), alkali (1–2 M), and salt (5 M) solutions.

The maximum replacement of anions in tellurides requires 36 h at a concentration of 0.8–0.9 M.[150,151]

IX. Carbon anion-exchange materials

Activated carbons show both cation exchange and anion exchange properties. Carbon obtained by heating saccharose acquires its maximum basic strength after heating to 400 °C.[7] The values of the capacity obtained by titrating with benzoic, acetic, and hydrochloric acids are 48.2, 26.5, and 0.43 mmol g^{-1} respectively.

To increase the basic strength of carbons, various methods of activating their surface have been studied. A remarkable feature is that the greatest number of basic centres was observed for specimens heated at 800 °C.[7]

Both the acidic and the basic properties of activated carbons are determined by the presence of oxygen groups on their surface. In a study of the acid–base properties of carbons obtained by oxidising swollen graphite in a liquid phase with hydrogen peroxide, a correlation was observed between the composition of the liquid phase and the ratio of the acidic and basic centres. This ratio can vary over a wide range; the anion exchange capacity for the lowest concentration of acidic centres is ~2 mequiv g^{-1}. Significant suppression of the acidic groups could not be achieved.

The number and ratio of the acidic and basic centres may change by a factor of several tens with change in the oxidising agent.[153]

With increase in the oxidation time, the concentration of both basic and acidic groups on the surface of carbon oxidised by nitric acid or potassium dichromate increased; the number of basic groups on unit surface area remained approximately unchanged[154] (Table 9).

Table 9. Dependence of the concentration of basic centres on the surface of oxidised carbon, heated at 800 °C, on the oxidation time.[154]

Concentration of basic centres	Oxidation time, h					
	0	0.5	1	2	4	6
Quantity, mmol g^{-1}	94	149	164	173	208	210
Surface concentration, centre nm^{-2}	0.54	0.58	0.53	0.54	0.58	0.45

The basic groups on the surface are carboxyl, lactone, phenol, carbonyl, and pyrone groups. On thermal treatment the carboxyl, carbonyl, and phenol groups decompose readily, whereas the number of lactone groups changes to a much smaller extent. The number of basic groups increases approximately ten-fold on heating, but increase in the treatment temperature above 800 °C leads to a decrease in their number.

X. Other anion exchangers

There are a number of compounds which do not belong to the above groups or which are amphoteric but show clearly defined basic character, at least under certain conditions.

Thus a new anion exchanger which shows its properties in neutral and in basic media and which is formed by the reaction of aluminium ions with 2,2′,2″-nitrilotri(ethanol) has been described.[155]

In it, two molecules of 2,2′,2″-nitrilotri(ethanol) are combined with one aluminium atom, but the molar ratio nitrogen : aluminium is always equal to 3. The formula and structure of the substance have not been established. Strictly speaking, this compound cannot be described as "inorganic". Anion exchange properties are also shown, however, by the substances obtained by heating it at temperatures up to 300 °C. This anion exchanger has an exchange capacity of about 1 mequiv g^{-1}, which correlates with the concentration of $-\overset{|}{\underset{|}{N^+}}-$ groups. It is stable in neutral and alkaline (2 M) solutions, but decomposes readily in acidic solutions. The anion exchanger has a particular affinity for the hydroxide ion. Other anions can be arranged in the following order:

$$CrO_4^{2-}>PO_4^{3-}>SO_4^{2-}\gg Cr_2O_7^{2-}>S_2O_3^{2-}>$$
$$>S_2O_8^{2-}>IO_3^-> MoO_4^{2-}\approx Fe(CN)_6^{3-}\approx SO_3^{2-}\geqslant HSO_4^- >$$
$$>AsO_2^-> Cl^-> BrO_3^-> Fe(CN)_6^{4-}> AsO_3^{3-}\approx SCN> Br^-> I^-.$$

The selectivity can be altered slightly by changing the pH and composition of the liquid phase. Equilibration is fairly rapid, and takes several minutes.

The following compounds with anion exchange properties have been used: polyantimonic acid, hydrated tin oxide, and hydrated titanium oxide.[156] These compouunds are produced industrially as anion exchangers. Their capacity is fairly low, 0.2–0.5 mequiv g^{-1}. None of the ion exchange processes studied is truly reversible, and in some cases, in particular in the case of iodide ions, the process is most probably not exchange but simply addition. The selectivity series for the compounds studied are approximately the same:

$$SO_4^{2-}\gg Cl^-> I^-> Br^-> NO_3^-.$$

These compounds are stable both in basic and in acidic (0.1 M) media, but they are dehydrated at about 130 °C when heated in air. All the substances studied have a large number of cation exchange centres.

The exchange capacity of hydrated cerium oxide[137] decreases with increase in the temperature of drying, possibly due to a decrease in the specific surface. The following selectivity series has been obtained for this compound:

$$ClO_4^-< Br^-< BF_4^-< NO_3^-< Cl^-< F^-.$$

Anion exchange on the hydrated oxides studied by different authors[122,123] was carried out in neutral and weakly acidic media, since hydrated oxides are mainly amophoteric, and are generally unstable in acidic media. The properties of hydrated oxides depend markedly on the method of synthesis.

Hydrated tin oxide[157] is stable to nitric and sulphuric acid solutions. Its anion exchange capacity reaches 2 mg-equiv g^{-1} (cation exchange capacity 1.5 mg-equiv g^{-1}), and the selectivity series is

$$I^-< Br^-< MoO_4^-< Cl^-< Fe(CN)_6^{3-}< Fe(CN)_6^{4-}<$$
$$<Cr_2O_7^{2-}< SO_4^{2-}< CrO_4^{2-}< PO_4^{3-}.$$

The use of amophoteric ion exchangers for absorbing and separating anions does not require their additional treatment. In some cases, however, the presence of acidic centres is quite inadmissible. It is then necessary, before using the anion exchanger, to "poison" the acidic centres using a strong base, for example KOH solution. This process, however, like any ion exchange process, is reversible, and when an ion exchanger of this kind is used it is necessary to control the reverse transfer of base to the liquid phase.

Transition metal phosphates, in particular zirconium phosphates, are widely known as cation exchange materials.[6] The properties of zirconium phosphate as an anion exchanger have been much less extensively studied.[158] Anion exchange properties are also shown by salts of antimonic acid, arsenic acid, and heteropolyacids.[159]

The ion exchange properties of ferrocyanides and cyanides in general are fairly widely known.[2,6] Mainly their cation exchange properties have been studied, however, although there are reports that certain cyanides act only as anion exchangers.[6]

It has been suggested that basic properties should be shown by cyanides containing metal cations in different oxidation states.[160] Methods for obtaining the anion exchangers $[Zn_2Co(CN)_6]OH$ and $[Zn_2Fe(CN)_6]OH$ have been described in detail,[161] and some of their properties studied. The structure of these compounds is very similar to that of double hydroxides. Cyanides, however, have a rigid hexgonal structure, so that they are excellent molecular sieves, capable of separating various organic molecules. The anion exchange capacity of $[Zn_2Co(CN)_6]OH$ is 2.5–2.7 mmol g^{-1}, and the number of acidic centres is low. These anion exchangers are extremely promising, but they have not yet been studied in detail.

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