6.1 Ore preparation

The metallic ore must be concentrated with respect to the metal to be extracted to facilitate the subsequent extraction process. This is achieved by subjecting the ore to a series of comminution (crushing and grinding), screening and separation operations.

6.1.1 Comminution processes

The comminution processes involve crushing the ore into fine particles to aid separation of the metal-bearing components (value) from the unwanted gangue. The reduction ratios (entry size: exit size) vary usually between 3:1 to 4:1. Thus, depending on the final size required there are a series of crushing operations using primary, secondary and tertiary crushers, with a final grinding or milling operation if a very fine particle size is required, e.g. 6 mm for sintering or less for froth flotation separation or pelletising. Owing to the fact that some fines are produced with each crushing operation irrespective of the reduction ratio a screening operation is used between each crusher, removing the fines which would not be further reduced in subsequent crushing or grinding operations. Various types of crushers and milling operations are shown in *Fig. 6.1.*

6.1.2 Classification processes

The first stage of separation of value from gangue is by classification which separates different particles due to their different rates of travel through a fluid (normally water). Therefore, the particles will be separated due to their different densities, sizes and shapes. Normally, the lighter gangue particles will be collected as 'tailings' in an overflow from the classifier while the denser metal-bearing particles will be collected as an underflow from the bottom of the classifier. Both portions will exist as a pulp of

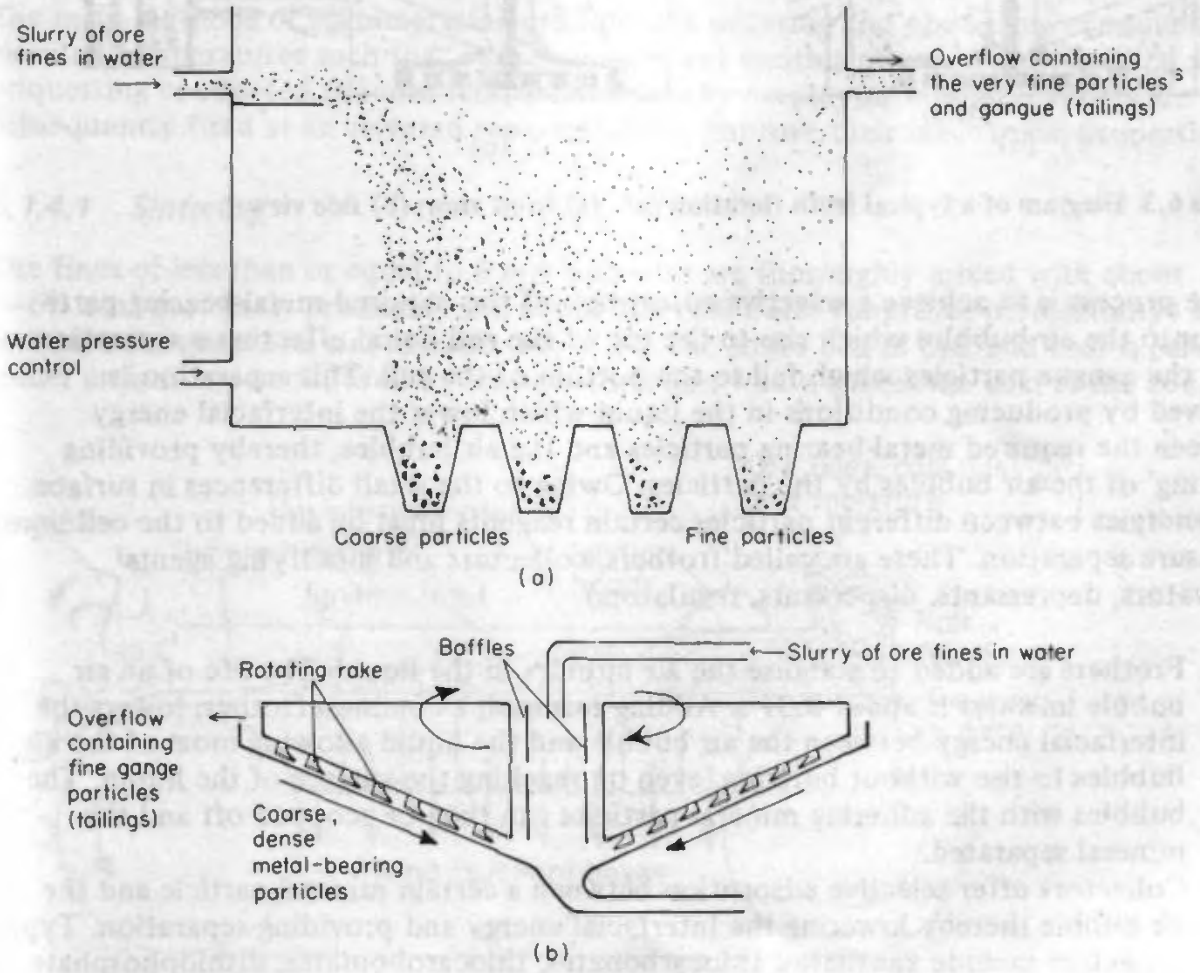

Figure 6.2 Diagrams of: (a) simple sluice box classifier and (b) a bowl or rake classifier

minerals in the water. A prolonged dwelling time in a fluid is required to separate the mineral particles from the water in the pulp when the ore has been finely ground. This is normally provided by a 'thickener' which is also used to reclaim the fluid from the pulp produced after grinding or to concentrate the solids in the pulp. Two types of classifier are shown diagrammatically in *Fig. 6.2.*

6.1.3 Separation processes

As classification is only a rough separation process further separation of the different mineral particles is required. This is achieved using the different physical properties of the various particles present, such as magnetic, electrical conductivity and surface properties. By far the most sensitive and most important separation technique is that of froth flotation which uses the difference in surface free energy of the particles (Section 4.2). Air bubbles are introduced into a cell containing the different mineral particles in water (pulp) and the fluid stirred to increase bubble formation (*Fig. 6.3*). The main aim

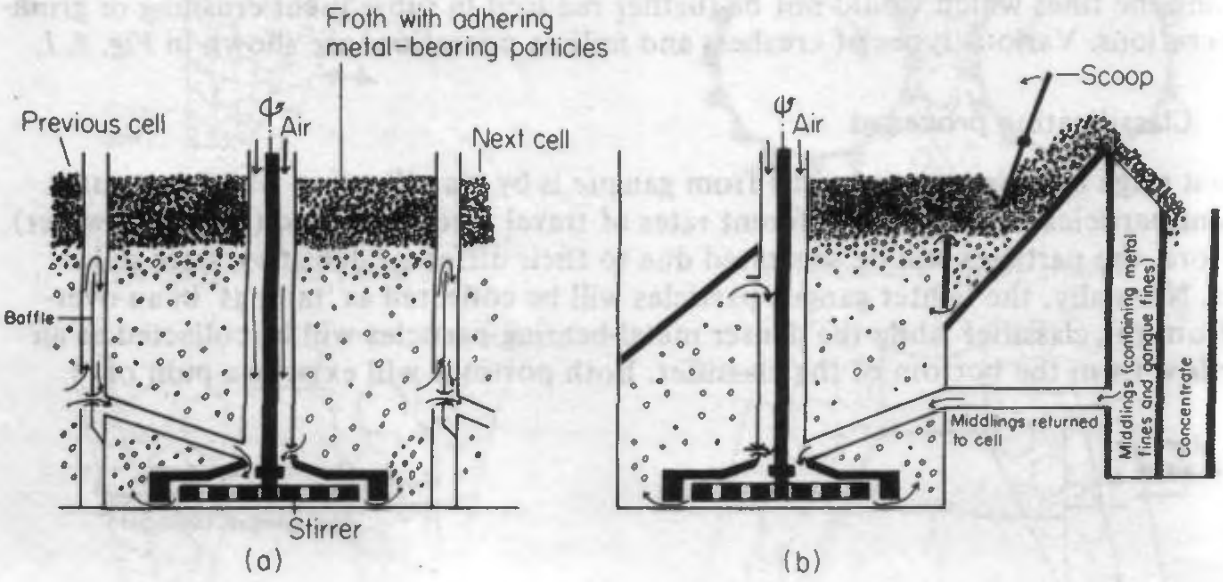

Figure 6.3 Diagram of a typical froth flotation cell: (a) front view; (b) side view

of the process is to achieve a selective adsorption of the required metal-bearing particles onto the air bubbles which rise to the top of the cell liquid effecting a separation from the gangue particles which fall to the bottom of the cell. This separation is achieved by producing conditions in the liquid which lower the interfacial energy between the required metal-bearing particles and the air bubbles, thereby providing 'wetting' of the air bubbles by the particles. Owing to the small differences in surface free energies between different particles certain reagents must be added to the cell liquid to ensure separation. These are called frothers, collectors and modifying agents[1] (activators, depressants, dispersants, regulators):

(i) Frothers are added to stabilise the air bubbles in the liquid. The life of an air bubble in water is about 0.01 s. Adding terpinol, a common frother, lowers the interfacial energy between the air bubble and the liquid allowing most of the air bubbles to rise without bursting, even on reaching the surface of the liquid. The bubbles with the adhering mineral particles can then be scooped off and the mineral separated.

(ii) Collectors offer selective adsorption between a certain mineral particle and the air bubble thereby lowering the interfacial energy and providing separation. Typical collectors include xanthates, thiocarbonates, thiocarobomates, dithiophosphates, used to float sulphide particles; fatty acids and soaps used to separate oxides; and amines used to separate silicates.

(iii) Modifying agents intensify the action of the collector by either decreasing (activators) or increasing (depressants) the interfacial energy between a mineral particle and the air bubble, thereby increasing the selectivity of the process. Regulators control the pH of the solution preventing precipitation of compounds in the liquid which might seriously affect the separation efficiency. The addition of reagents to the cell liquid is carried out before or during the flotation process and is termed 'conditioning'. Only a few parts per million of total reagents are required to provide efficient froth flotation but most mineral particles must be ground between 200×10^{-3} mm and 5×10^{-3} mm and diluted to between 25–45% with water (pulp). Flotation cells are usually arranged in series with the liquid continuously passing from one cell to the next. The size of each cell depends on the total flotation time required and the space and handling arrangements available.

6.1.4 Agglomeration processes

Agglomeration is the reforming of fine particles into larger lumps and is usually conducted if:

(i) the separation requirements of an ore necessitate grinding and froth flotation and the particles produced are too fine to be added directly to a reverberatory or blast furnace;
(ii) a rich ore is too dense to be efficiently reduced due to poor reducing gas–solid ore contact. Grinding the dense ore and reforming it into a more porous material of appropriate sized lumps improves the efficiency of the subsequent smelting process.

The main methods of agglomerating ore fines are sintering and nodulising conducted at elevated temperatures such that partial or incipient melting occurs, and pelletising and briquetting conducted at room temperature usually employing a binder. Pellets are subsequently fired at an elevated temperature to improve their mechanical properties.

6.1.4.1 Sintering

Ore fines of less than or equal to 6 mm diameter are thoroughly mixed with about 5–6% coal dust (heat producer) and about 10–12% water (improves permeability) and fed onto the grate of a sinterstrand (*Fig. 6.4*). The sinter bed of ore, and coal is passed under an ignition hood, fired by oil or natural gas, which ignites the coal in the bed.

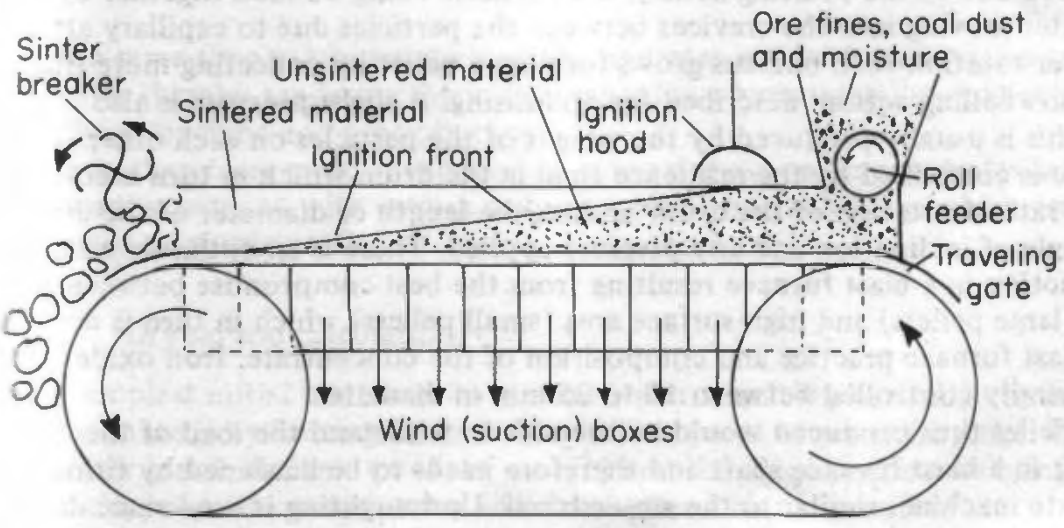

Figure 6.4 Diagram of a sinterstrand using downdraughting

The heat or ignition front is sucked down through the bed as it passes over several suction or wind boxes. The aim is to complete the sintering by the last but one wind box; the last wind box being used for cooling the sinter. The sinter is finally broken up into conveniently sized lumps.

The sintering process occurs in two stages:

(i) Calcination during which decomposition and drying take place removing H_2O, CO_2, SO_2 and also removing any volatile metals, e.g. Cd, As. These may be recovered with appropriate gas cleaning plant from the flue gases.

(ii) Incipient fusion during which the surface of the ore fines partially melts and the liquid is drawn into the interstices between the ore fines by capillary action. This increases the strength of the sinter.

Sintering is used for agglomeration of oxide and sulphide concentrates. The main difference is that in sintering sulphide ores updraughting (air blowing) rather than downdraughting (air being sucked through the bed) is used after ignition so that sulphur dioxide can be collected more easily and reprocessed to elemental sulphur or sulphuric acid. Sintering sulphide ores also provides a roasting operation in which the metal sulphides are converted to oxides.

6.1.4.2 Nodulising

Ore fines, coal dust and moisture are again thoroughly mixed and fed into a rotating drum at an elevated temperature—similar to that used for sintering. The rotating action and high temperature result in the formation of nodules in the same way that snowballs are produced by rolling snow flakes. However, due to the poor control over temperature, the lower melting point constituents of the concentrate tend to fuse resulting in irregularly shaped nodules of low permeability. For this reason nodulising is normally only used for agglomerating metallic fines produced from smelting, polishing and machining operations in the production of secondary precious metals (Section 7.2.2.7) where low melting point gangue constituents are not present.

6.1.4.3 Pelletising

Ore fines of less than about 0.20 mm are unsuitable for sintering due to the danger of complete fusion of such a small particle. These ore fines are thoroughly mixed with 10% water to improve permeability and a binder such a bentonite, lime, salts or organic material, and fed into an inclined rotating drum or disc. A nucleus of a number of fines is produced due to the rotating action, the particles being bonded together by the binder and water moving into the crevices between the particles due to capillary attraction. On further rotation each nucleus grows forming a pellet by collecting more fines in a similar 'snowballing action' described for nodulising. A slight pressure is also required but this is usually produced by the weight of the particles on each other. The final pellet size is controlled by the residence time in the drum which in turn is controlled by the rate of rotation of the drum or disc, the length or diameter of the drum or disc, the angle of inclination and any pressure applied. There is an optimum size of pellet for reduction in a blast furnace resulting from the best compromise between high permeability (large pellets) and high surface area (small pellets) which in turn is dependent on the blast furnace practice and composition of the concentrate. Iron oxide pellets are generally controlled between 10 to 25 mm in diameter.

The green pellet thus produced would be too soft to withstand the load of the charge above it in a blast furnace shaft and therefore needs to be hardened by firing on a travelling grate machine, similar to the sinterstrand. Updraughting is used since downdraughting would cause crushing of the soft green pellets. Alternatively, the green pellets may be fired in a small shaft furnace.

6.1.4.4 Briquetting

Ore fines are mixed with a similar binder material as that used for pelletising and mechanically pressed at room temperature. The briquetting may be subsequently hardened in a tunnel kiln. In some cases a binder is not necessary. Hot briquetting is also being used to a limited extent, mainly in the reprocessing of metal-bearing particles in flue dusts. Owing to the excessive wear on the press, briquetting tends to be an expensive process and has limited application.

The choice of pellet or sinter charges in blast furnace reduction processes depends on the composition of the ore, the permeability of the agglomerate and the total processing costs.

Generally pellets offer better reducibility than sinter during reduction smelting in a blast furnace due to the more favourable distribution of porosity in the pellets. The majority of the pores are concentrated at the surface of the pellet and therefore provide very high areas of contact initially at the lower temperature. When the pellet has been reduced at its surface the higher temperatures available lower down the blast furnace stack somewhat compensate for the reduced area of contact compared with sinter which has a more uniform distribution of porosity. Sintering provides favourable chemical effects such as the elimination of CO_2 and sulphur as SO_2 but sinter has a very low thermal efficiency due to the large amounts of air needed to be heated up and drawn through the sinter bed (air has a high specific heat–Section 2.1.4.1). Also, because of the finer particles required for pelletising, the preceding separation process will be more efficient, usually resulting in a higher metal content than in sinter. However, in both cases the increased comminution and agglomeration costs have to be justified by an increase in the production of metal.

The addition of a flux material in the sinter or pellet mix will provide a self-fluxing agglomerate.

6.2 Pyrometallurgical extraction processes

Metal sulphides, carbonates, hydrates and basic carbonates are not normally convenient starting materials for the extraction of the metal. Most metal sulphides are not reduced with carbon or hydrogen, the most common and readily available reducing agents, since CS_2 and H_2S have less negative values for $\Delta G^{\ominus}$ of formation (*Fig. 2.13*) than most metal sulphides. For instance,

$$2Cu_2S + C \longrightarrow 4Cu + CS_2 \qquad \Delta G^{\ominus}_{1100\,^{\circ}C} = +160 \text{ kJ mol}^{-1}$$

$$Cu_2S + H_2 \longrightarrow 2Cu + H_2S \qquad \Delta G^{\ominus}_{1100\,^{\circ}C} = +130 \text{ kJ mol}^{-1}$$

At the same time sulphides, carbonates, hydrates and basic carbonates are not soluble in water thereby rendering them unsuitable for a hydrometallurgical extraction route involving leaching and precipitation.

It is, therefore, more convenient to convert these ore concentrates into oxides which are readily reduced with carbon or hydrogen, or into sulphates which are soluble in water or sulphuric acid.

6.2.1 Drying and calcination

The simplest initial treatment to remove water which is physically combined with the concentrate is by heating to above the boiling point of water (drying). The evaporation of water is endothermic (+44 kJ mol^{-1}) and thus requires heat to bring the mineral to the appropriate temperature and for the evaporation process.

Calcination involves the chemical decomposition of the mineral and is achieved by heating to above the mineral's decomposition temperature (T_D) (Section 2.2.3.10) or

6.3 Hydrometallurgical extraction processes

Hydrometallurgical extraction processes involve dissolving (leaching) the metal value from the ore, concentrate or process waste in an aqueous solution (leaching reagent) and subsequently precipitating or isolating the metal required to be extracted. The ore mineral may not be soluble in water necessitating a pretreatment such as a sulphatising roast producing a water soluble metal sulphate. Addition of acids, alkalis or certain salts to the water may also aid dissolution of the required mineral. The leaching process will usually take several minerals into solution and it may be necessary to first purify the leached solution by precipitation of certain unwanted compounds or metals prior to the precipitation or isolation of the required metal. Precipitation results in a metal or group of metals being thrown out of solution in a solid form while isolation techniques result in the preferential selection of a metal ion or group of metal ions in a suitable solvent.

Precipitation may be effected by pH control, addition of certain chemicals, simply cooling the solution, or by chemical reduction or oxidation. Isolation techniques include reverse osmosis, ion exchange and solvent extraction.

Electrolytic separation techniques are sometimes classified as hydrometallurgical processes but these will be dealt with in a separate section.

6.3.1 Leaching

Leaching involves dissolving the required metal in the concentrate in a suitable reagent usually taking many other metals also present in the ore into solution at the same time. The leaching reagent must be cheap and recoverable from the solution to aid the total process economics. Some typical reagents are listed in *Table 6.4*.

Table 6.4 SOME COMMON LEACHING REAGENTS USED FOR VARIOUS METAL BEARING MINERALS

Mineral	*Leaching reagent*
Metal oxides	H_2SO_4
Metal sulphates	H_2SO_4 or even H_2O
Metal sulphides	$Fe_2(SO_4)_3$ solution
Cu/Ni minerals	NH_3 solutions, NH_4CO_3–producing complex amines, e.g. $[Ni(NH_3)_6]^{2+}$
Al_2O_3	NaOH
Au, Ag	NaCN–producing complex cyanides, e.g. $Au(CN)_2^-$

The rate controlling steps in the leaching process are generally the transport of the reagent to and the transport of the leached solution away from the dissolution reaction site, rather than the dissolution reaction itself. Thus, the reaction kinetics of the leaching process are improved by increasing the diffusion rates of the reagent and leached solution through the pores of the mineral being leached; presenting the mineral in a fine particular form by prior crushing and grinding; providing increased agitation during leaching and increasing the temperature and pressure of the reaction. At the same time a high degree of crushing and grinding will aid any subsequent separation of the ore, thereby reducing the gangue content which may consume large quantities of the leaching reagent.

There are several different leaching methods used depending on such factors as required leaching rates, ore composition, subsequent isolation, precipitation or extraction process:

(i) Heap leaching is used when ore lumps of less than 200 mm diameter are stacked

in the open on drainage culverts and the leach reagent sprayed over the ore heaps. This is a slow process with low recovery rates.

(ii) Percolation leaching uses ore fines of about 6 mm placed in large tanks and percolated by a series of leach solutions increasing in concentration.

(iii) Agitation leaching uses ore fines of 0.4 mm diameter or less which would be unsuitable for percolation leaching. The fine ore particles are suspended in the leach solution and stirred mechanically or with compressed air jets. This is faster and more efficient than percolation leaching but is also more costly.

(iv) Pressure leaching at elevated temperatures is used to increase dissolution rates and to dissolve minerals which would be difficult to dissolve at atmospheric pressure. It also prevents dissolution of gangue components in certain cases. In this respect Ni, Co and Cu sulphides are dissolved in the presence of oxygen with ammonia solution between 71 and 87 °C at pressures of 7.1 to 10.5 (709.3–1064 kN m^{-2})[20]. The iron sulphide present in the ore is oxidised under these conditions and remains undissolved as ferric hydroxide ($Fe(OH)_3$). The solution containing the Ni, Co, and Cu as complex amines is first treated to precipitate the copper as Cu_2S by boiling at atmospheric pressure and after oxidation of the thiosulphates using air at 50 atm (5066.2 kN m^{-2}) pressure and 200 °C the nickel is precipitated by reduction with hydrogen.

The Bayer process treats impure bauxite ore with a strong caustic soda solution (130–350 g Na_2O/l) at 5–10 atm (506.6–1013.2 kN m^{-2}) pressure and between 150–170 °C. The aluminium is dissolved as the AlO_2^- anion,

$$Al_2O_3(\text{bauxite}) + 2NaOH \xrightarrow[8\text{ atm}]{160\,^\circ C} 2NaAlO_2 + H_2O$$

leaving iron, silicon and titanium oxides undissolved. Hydrated alumina, $Al_2O_3.3H_2O$, is precipitated on cooling and 'seeding' with pure $Al_2O_3.3H_2O$ crystals. Subsequent calcination at 1200 °C provides the pure alumina which is used in the fused salt electrolytic extraction of aluminium (Section 6.4.2).

(v) Bacterial leaching has been used to increase the leaching rates of sulphides by a factor which ranges between 10 to 100. In this respect the bacterium thiobacyllus ferro-oxydans has been used in the leaching of copper sulphide ores containing iron. The bacterium oxidises Fe^{2+} to Fe^{3+} preventing the dissolution of iron and, therefore, increasing the dissolution rate of the copper.

The leached solution in each case will contain several unwanted minerals which may hinder the extraction of the required metal and it may be necessary to purify the leached solution by precipitating some of these unwanted minerals prior to the precipitation or isolation of the main metal.

Leach or *in situ* mining in which a leaching solution is flushed through an ore body, is likely to become more popular for the very lean ores which are difficult to mine, e.g. uranium ores.

6.3.2 Precipitation techniques

6.3.2.1 Precipitation by pH and p_{O_2} control

The precipitation of a metal from an aqueous solution is largely controlled by the pH and partial pressure of oxygen of the solution. Thus, the thermodynamic relationships between the metal ions, hydrogen ions and oxygen present in solution provide the hydrometallurgist with a considerable amount of knowledge. Rosenqvist[21] has explained this relationship by considering all the reactions between a hypothetical metal Me, H^+ ions and O_2 pressure, when the metal forms cations Me^{2+} and Me^{3+}, anions MeO_2^{2-} and MeO_2^-, and solid hydroxides $Me(OH)_2$ and $Me(OH)_3$. Therefore, the following reactions are possible: