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METHOD FOR THE ALKALINE ROASTING OF
AN ACIDIC OXIDE ORECharles G. Maier, Los Altos, Calif., assignor to
Bennett Preble, Santa Rosa, Calif.No Drawing. Application August 7, 1944,
Serial No. 548,511

12 Claims. (Cl. 23—56)

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In a co-pending application (now Patent No. 2,394,793) Serial No. 548,512 filed August 7, 1944, a method of preparation for alkaline roast of ores containing refractory acidic oxides has been disclosed. This method consists in bringing about solid infusible associations of alkaline and alkaline earth hydroxy-carbonates with fine ground ore, to the end that the many mechanical difficulties of handling and roasting such ores in an alkaline environment may be avoided. In the present application I disclose improved methods of conducting the roasting process itself.

The original conception and discovery of the possibility of producing solid infusible associations of alkaline earth-alkali-hydroxy-carbonates had for its primary purpose the attainment of a suitable bond for spherulizing, agglomerating, or briquetting of ores with alkali carbonates, but when ores prepared in accordance with my co-pending application were roasted by conventional methods, unexpected, and at first, inexplicable, improvements in conversion were reached. Further experimentation and study have enabled me to rationalize the processes occurring, so that substantial improvements in the roasting technique could be made on a basis broader than corresponding merely to the mechanical improvements attendant upon the use of aggregates for ore charge.

In the alkaline roast of ores containing acidic oxides, such as chromium, titanium, zirconium, molybdenum, vanadium, tungsten, and in fact all oxides capable of assuming acidic properties when combined with three or more equivalents of oxygen, one of the chief difficulties experienced in the past has resulted from the fusibility of the alkali, and in many instances of the salts formed by the roast, as, for example, sodium chromates, molybdates, etc. It has long been a desideratum to secure a satisfactory roast at temperatures low enough definitely to avoid fusion of the alkali and the salts produced, but heretofore the only practical method of securing reasonable extractions as conversions in workable time of treatment has been to conduct the roast at temperatures over the melting point of the alkali carbonates used, while partially "drying up" the resultant fusion by the addition of alkaline earth oxides or carbonates.

The alkali most commonly used, sodium carbonate, melts at about 854° C. and if chromium be chosen as typical of an acidic oxide commercially extracted by this method, it is found that the melting point of sodium chromate is near 800° C. The melting point diagram of the so-

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dium chromate-sodium carbonate system has not been recorded in the literature. My observations indicate that the system is similar to that of sodium chromate-sodium sulphate, an isomorphous type without apparent melting point minimum. It is evident, then, that in seeking the objective of an alkaline roast for the production of chromates, without fusion of any of the salts in the system producing sodium chromate, initial roasting temperatures not over about 850° C., and final temperatures not over about 800° C. will be required. Similar, but of course, not identical figures will pertain to other salts such as molybdates, tungstates, vanadates, etc.

When the attempt is made to operate below these critical temperatures of fusion, inadequate conversions to salts of the acidic oxides, even after long roasting periods, have heretofore invariably been experienced. Thus Doerner (H. A. Doerner, "Roasting of Chromite Ores to Produce Chromates," U. S. Bur. of Mines Rept. Invest. 2999, June, 1930; also H. A. Doerner, "A Study of Methods of Producing Chromate Salts from Domestic Ores," Bull. V, Mining Exp. Station, State College of Washington, 1939) throughout an elaborate series of experiments in which the conditions of roasting were varied over wide limits and compositions, found that he could convert pure Cr_2O_3 to chromate at temperatures as low as 850° C., but required higher temperatures for chrome ores, ranging from 900° C. to 1050° C. Since chromates begin to decompose thermally at 1050° to 1100° C., no further increase of temperature is feasible. Even at these elevated temperatures, it was usually necessary to roast for periods of 8 to 12 hours.

The use of a catalyst to promote the oxidation of chrome ore in chromate roasting has been suggested. German Patent 163,814 mentions the use of the oxides of manganese, copper, or iron for this purpose. Laboratory test of such proposals shows that manganites and manganates, responsible for the catalysis, are themselves unstable above about 800° C. whence they can exert no chemical influence under conventional roasting conditions. In the presence of fused caustic alkali, manganates were formed at about 500–600° C., and possessed the power to oxidize chromite in turn, but such procedure seems of little practical importance because of the extraordinary corrosive action of fused caustic alkali at these temperatures in the presence of excess air and oxidizing salts. This prevents the construction of effective large scale equipment suitable for commercial use,

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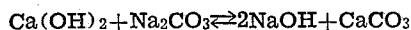
aside from further difficulties in the introduction of the requisite amounts of heat and air in the fused bath, and the complexity of separation of the manganese salts from the product. Thus the use of caustic alkali as such, while permitting salt formation with acidic oxides at lower temperatures, leads to further difficulties because the alkali itself melts at still lower temperatures, and only increases the trouble with fusion and corrosion.

The essence of my present invention is the discovery of a practical means of bringing about incipient, but limited caustic formation, at roasting temperatures, whereby the lower temperatures of salt formation can be realized without fusion, and without involving the presence of sufficient free caustic alkali at any period of the roast in quantities permitting partial liquefaction.

There are two ways in which I can bring about controlled, incipient caustic formation at roasting temperatures that are related chemically, but somewhat different in practice.

In the first variation of my method, I introduce into a charge of fine ground acidic oxide ore containing sufficient anhydrous alkali carbonates to be stoichiometrically equivalent to the total content of acidic oxides, a quantity of an alkaline earth hydroxide. I may, if desired, add a limited quantity of water during an ore preparation step, in accordance with my copending application, whereupon I achieve a hardening or set due to the formation of infusible associations which I term herein and in the claims as hydroxy-carbonates of alkalis and alkaline earths. As far as the roasting itself is concerned, preparation in the form of spherules, briquettes, or other type of aggregate is advantageous but not essential.

Whether I have a spherulized charge, or merely a mixture, this combination acts as an infusible reservoir or buffer for caustic alkali. The conventional causticizing reaction



is, of course, only incipient in either of these instances, but as soon as the small quantity of caustic alkali present due to contact is utilized for salt formation with acidic oxides during the roast, more can form, yet there is never enough free caustic present at any time to entail the risk of fusion at any temperature below the melting point of the salt formed.

In practicing this method, I find it advantageous not to permit the roasting temperature to rise too high, since it is undesirable to bring about too rapid loss of hydroxyl or hydrate water. The first step in my roasting process is, in effect, a causticizing reaction conducted between solid reactants, and it is undesirable to decompose the alkaline earth hydroxides too rapidly, as they will undoubtedly do under heat alone if separated from this environment.

As explained in my copending application, when I prepare a spherulized charge, it is dried at a maximum temperature of 300° C., at which point the free water, but virtually none of the hydroxyl or hydrate water, is driven off. The roasting that is most effective according to the present method occurs between 300° C. and 800° C. for chromate formation, or whatever other upper limit that may be imposed by the melting point of salts that are formed from other ores. The best furnace capacity is usually obtained when the temperature of the roast is between

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700° C. and 800° C. Above 350° C., aside from the mechanical difficulty of fusion of salts formed, there is usually an actual diminution of rate because of enhanced resistance to oxygen penetration in the semi-fused state.

The solid causticizing reaction is doubtless promoted by increase of temperature, since caustic alkalis are more stable towards thermal dissociation than alkaline earth hydroxides.

This variation of my method would not in any case be effective if applied at conventional temperatures of 900-1050° C., since rapid heating to this temperature would drive off water from the alkaline earth-alkali hydroxy-carbonates, before reaction with acidic oxides could occur: under these circumstances the charge would revert to a conventional mixture of calcined oxides and carbonates, having no advantage over the usual practice.

In the second variation of my roasting method, which I utilize especially advantageously when the presence of alkaline earths in the residue or converted roast is objectionable for reasons connected with subsequent leaching or other treatment, I bring about incipient and controlled causticizing in the solid charge by means of the hydrolytic action of water vapor at roasting temperatures.

The reaction



is, of course, one that proceeds nearly completely to the left under ordinary conditions. I have found, however, that at roasting temperatures, and in the presence of acidic oxides that can act as "acceptors" of the alkali formed, the reaction can proceed to the right to an extent suitable as a source of alkali, again without permitting enough caustic to form so that fusion could occur. Since water is ultimately evolved when the alkali is accepted by the acidic oxides to form a salt, it is proper to term the action of water vapor or steam catalysis through a hydrolytic mechanism.

In some instances an oxygen carrying catalyst, such as oxides of manganese, may also be included in the roast charge, since, because of the lower roasting temperatures attainable by the hydrolytic catalysis, I am also able to utilize the oxygen carrying power of such substances as manganites and manganates without subjecting them to thermal decomposition. It should be noted, however, that a complete list of catalytic oxides capable of acting as oxygen carriers would include many of the acidic oxides for the treatment of which the roast is conducted, namely chromium, molybdenum, vanadium etc. All that is necessary for such catalytic activity is that the acidic oxides exist in two or more valence states each capable of combining with alkali, the effectiveness as catalyst being a function of the relative concentrations of the two forms that may co-exist. In the strictest sense, the process as here described should probably be considered auto-catalytic, and some experimental evidence is available indicating that it is actually so in that it proceeds at an enhanced rate after initial reaction, when the hydrolytic catalysis precedes.

Having disclosed the principles of my invention, I shall illustrate the specific details of the manner of its application by reference to several typical examples of methods used for the alkaline roast of a beach sand concentrate containing values in chromium, titanium, and zirconium.

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Example 1

A charge containing 600 pounds of sand concentrates, ground to pass a screen of 200 meshes per inch, with 320 pounds of commercial hydrated lime (calcium hydroxide) and 280 pounds of soda ash is prepared in accordance with my co-pending application as spherules of an average diameter of $\frac{3}{4}$ inch, utilizing 30 gallons of water, and is hardened and set at a maximum temperature of 300° C.

The aggregate is roasted in any conventional type of retort furnace, either externally or internally fired, for a period of 2 hours at an average temperature of 800° C., the maximum at any time not exceeding 850° C. During the roasting period, an amount of air equivalent to not more than 10 times that stoichiometrically necessary to satisfy all oxygen absorbing oxides in the ore is passed through the bed of aggregate in the retort. The air is preferably preheated to prevent cooling of retort and charge.

The amount of air utilized is important. My experiments show an oxygen utilization efficiency of 15 to 25%. Under the best conditions, the air should be from 4 to 7 times theoretical. Too great an excess of air tends to promote the dissociation of $\text{Ca}(\text{OH})_2$ and hydroxy-carbonates before they can finally react in the acceptance of acidic oxides, so that the process tends to degenerate to the conventional method with alkaline earth oxides. Too little air is also deleterious, in that inadequate oxidation may ensue, resulting in the salts of some acidic oxides in a lower state of oxidation, as for example, sodium and calcium chromites, which are relatively insoluble, and of no commercial value.

The result of this procedure and method is virtually complete conversion of all the chromium, titanium, and zirconium to the form of the corresponding sodium salts of these acidic oxides. To obtain a similar result by conventional methods, using calcium oxide or carbonate in a bedded charge would require periods of roasting from 8 to 12 hours at temperatures of 950–1050° C. and would entail serious fusion difficulties. As conducted by the disclosed method at 800° C., no fusion or sticking of the charge occurs; refractory problems are minimized, and substantially only sodium salts of the acidic oxides are produced.

Example 2

A charge containing 600 pounds of sand concentrates as in Example 1, is spherulized with 60 pounds of commercial calcium hydroxide and 280 pounds of soda ash, using 16 gallons of water. The spherules, of $\frac{3}{4}$ " average diameter, are set and dried at a maximum temperature of 300° C. as before.

This charge is roasted in a rotary kiln of conventional design adjusted to pass the spherules through the reaction zone of the kiln, controlled at a temperature of 700–800° C., in a residence period of 3 hours. The time period is obtained by a relatively high slope and low speed of rotation, rather than by a low slope and a high rate of kiln rotation. Because the charge has unusually high porosity, high rotation speeds are not necessary for contacting the charge with furnace gases, and a low speed is desired to avoid attrition action by the moving spherules. The kiln may advantageously be filled nearly to the diameter.

The firing of the kiln is by means of a steam actuated oil burner, not only for the purpose of limiting the maximum flame temperature, secur-

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ing a long soft flame; but also to supply water vapor over and above that arising from the combustion of the hydrocarbon fuel. The amount of steam used is controlled, along with the kiln draft, so that about 5 times the theoretical air necessary for combustion plus the oxygen requirements of the charge is passed while maintaining the water vapor content of the flue gases as near 20–25% by volume as may be feasible with the combustion space available. This will usually require some excess steam over that normally used in a burner of the type mentioned.

The result of this roasting procedure again is substantially complete conversion of acidic oxides to sodium salts. This result has never been approached or duplicated in previous practice, since an authoritative investigator (Doerner) has reported the rotary kiln unusable at conventional operating temperatures.

Example 3

A charge of 600 pounds of sand concentrates, as in previous examples, is admixed with 280 pounds of soda ash, and roasted in a conventional multiple hearth furnace, with a maximum temperature on the middle hearths of 800° C., and an average temperature of 750° C. On the lower hearths, steam operated air injectors of the jet type supply air at a rate 4 times the theoretical air (oxygen) requirements of the charge. The furnace is preferably fired by hydrocarbon fuels, and the injectors are adjusted so that the water vapor content of the flue gases reaches 40–50%. The rate of rabbling is controlled so that the charge passes the hearths that are at temperatures above 650° C., and below 800° C., in a residence time of 2.5 hours.

If 60–75 pounds of oxides of manganese (non-siliceous manganese ores may be used) are added to the charge, the residence time may be reduced to $1\frac{3}{4}$ to 2 hours, other conditions remaining unaltered.

This procedure also furnishes substantially complete conversion of all contained acidic oxides to sodium salts, and makes possible effective conversion without alkaline earth additions to the charge, below the temperature of fusion—a desideratum that has long been sought by investigators of this art.

The principles that have been disclosed can be applied in still other ways, or in forms intermediate between the illustrative examples given. Thus, in Example 1, steam may also be introduced for the purpose of retarding the thermal decomposition of the hydroxy-carbonates. This increases the rate of conversion by a factor of about 1.25, allowing treatment times of 1 hour 40 minutes. In general, however, steam will be uneconomic as compared to the use of alkaline earth hydroxides except in those instances where subsequent treatment, especially the leaching of roast product, can be materially simplified when alkaline earths are absent. Many of the ores of acidic oxides contain substantial contents of alkaline earths as part of the constitution.

The alkaline earth hydroxides, and the conversion product termed hydroxy-carbonate, furnish water vapor upon reaction with acidic oxides, and to some extent, by spontaneous thermal decomposition. It is plain that another version of Example 1 includes the use of a closed retort, retaining pressures above atmospheric. In this instance oxygen may be supplied, rather than air, at a pressure slightly greater than the "blow off" pressure of the retort. In this instance the tem-

perature may be reduced to 600–700° C. when operating at about 2 atmospheres pressure, and to still lower temperatures at still higher pressures.

The use of steam per se, or oxygen carrying catalysts are not as effective in promoting the roast, however, as the hydroxy-carbonate combination: these former substances merely add a percentage (15–35) to the rate of conversion, whereas the latter, and the method of ore preparation of my co-pending application, result in a five to seven-fold increase of rate of conversion at temperatures more than 200° lower than conventional practice.

In this connection, I have discovered a chemical reason for the beneficial effect of lime itself, over and above its function as caustic buffer constituent. Microscopic examination of chromite crystals roasted in the presence of sufficient lime, and after removal of substantially all of the contained chromium oxide as alkali chromate, show black crystals pseudomorphic with the original. If, on the other hand, no lime is present, the crystals are less well defined in form after conversion, and are reddish brown in color. Further chemical examination indicates the black product to be a lime-iron spinel, whereas the brown crystals are essentially ferric oxide, although sodium ferrite may be present if alkali is slightly in excess of stoichiometric requirements of the acidic oxides. The basic roast of chromite is then in effect a process of spinel interchange or metamorphosis in the presence of lime: in the formula $\text{FeO}:\text{Cr}_2\text{O}_3$ the FeO is replaced by CaO , itself being oxidized, and in turn replacing the chromium oxide, forming $\text{CaO}:\text{Fe}_2\text{O}_3$. These steps are doubtless closely tied together chemically, the possibility of each step being dependent on the progress of the other.

Thus, the nature of the residual iron after alkaline roast may be reason, at times, for selecting a specific version of my method. The use of lime, or other alkaline earth, accelerates the roast, but puts the residual iron in place of the chromium locked in a spinel structure, hence in a form of little value as an iron source. If the recovery of iron from chrome or titaniferous magnetites is the objective of subsequent treatment, the choice of method may advantageously be for the low lime, or lime-free roast catalysed with water vapor.

It is clear that the method of this invention is not limited to a specific type of roasting equipment; the latter may be a matter of choice while maintaining the fundamental principles of my method of producing an incipient caustic alkali formation, without fusion or partial lignefaction, and involving only solid, or solid and gaseous, constituents.

I claim:

1. A process for the alkaline roasting of an acidic oxide containing ore comprising mixing dry, finely divided ore with an alkaline earth hydroxide and an alkali metal carbonate, the quantity of said hydroxide being at least 10% on the weight of the ore, the quantity of said alkali metal carbonate being substantially equivalent to that required stoichiometrically to combine as normal alkali salt with the total content of all acidic oxides present in the ore, adding sufficient water to the mixture to enable it to be formed into discrete agglomerates, forming the wet mixture into discrete agglomerates, drying the coarse agglomerates at a temperature below about 300° C. to form a hydroxy-carbonate of the alkaline

earth and the alkali metal which bonds the ore particles together into agglomerates, roasting the agglomerates at a temperature between 300° C. and 800° C., and supplying oxygen to the roast in a quantity between about four times and less than about ten times that required stoichiometrically to form an alkali metal salt with the acidic oxide under the conditions of the roast.

2. The process of claim 1 wherein the ore is a chrome oxide ore and the temperature of the roast is between 700° and 800° C.

3. A process for the alkaline roasting of an acidic oxide containing ore comprising mixing dry, finely divided ore with an alkaline earth hydroxide and an alkali metal carbonate, the quantity of said hydroxide being about 50% on the weight of the ore, the quantity of said alkali metal carbonate being substantially equivalent to that required stoichiometrically to combine as normal alkali salt with the total content of all acidic oxides present in the ore, adding sufficient water to the mixture to enable it to be formed into discrete agglomerates, forming the wet mixture into discrete agglomerates, drying the coarse agglomerates at a temperature below about 300° C. to form a hydroxy-carbonate of the alkaline earth and the alkali metal which bonds the ore particles together into agglomerates, roasting the agglomerates at a temperature between 300° and 800° C., and supplying oxygen to the roast in a quantity between about four times and less than about ten times that required stoichiometrically to form an alkali metal salt with the acidic oxide under the conditions of the roast.

4. The process of claim 3 wherein the ore is a chrome oxide ore and the temperature of the roast is between 700° and 800° C.

5. A process for the alkaline roast of an acidic ore comprising mixing said ore in finely ground form with the substantially stoichiometric equivalent quantity of alkali carbonate and in the absence of other than naturally contained alkaline earths, roasting the mixture at a temperature between 300° and 800° C., continuously supplying to the roast an amount of water vapor at least theoretically sufficient to induce substantially complete hydrolysis of the contained alkali carbonate to alkali hydroxide, and supplying oxygen to the roast in a quantity between about four times and less than about ten times that required stoichiometrically to form an alkali metal salt with the acidic oxide under the conditions of the roast.

6. The process of claim 5 wherein the ore is a chrome oxide ore and the temperature of the roast is between 700° and 800° C.

7. In the alkaline roasting of an acidic oxide ore, the step of roasting a mixture of the ore with an alkali metal carbonate and a material for reacting with said carbonate to form alkali metal hydroxide under the conditions of the roast at a temperature between 300° and below about 850° C., and supplying oxygen to the roast in a quantity between about four times and less than about ten times that required stoichiometrically to form an alkali metal salt with the acidic oxide under the conditions of the roast, the quantity of said alkali metal carbonate present in the mixture with the ore being substantially equivalent to that required stoichiometrically to combine as normal alkali salt with the total content of all acidic oxides present in the ore, the material being selected from the group consisting of water and alkaline earth hydroxides, the quantity of the material being sufficient theoretically to induce

substantially complete conversion of the alkali metal carbonate present to alkali metal hydroxide.

8. The process of claim 7 wherein the mixture is free of other than naturally contained alkaline earths, and the water is supplied in an amount at least theoretically sufficient to induce substantially complete hydrolysis of the contained alkali carbonate to alkali hydroxide.

9. The process of claim 7 wherein the material is lime.

10. A process for roasting an ore comprising mixing acidic oxide ore with (1) sodium carbonate stoichiometrically equivalent to the total acidic oxides in the ore and (2) a small quantity of lime, roasting the mixture in the presence of water available to convert the sodium carbonate to sodium hydroxide and at a temperature between 300° and 800° C., and passing into the mixture during the roasting air sufficient to satisfy the oxygen demand of the oxygen absorbing oxides in the ore and less than ten times that required stoichiometrically to satisfy said demand.

11. A process for roasting an ore comprising mixing an acidic oxide ore with (1) sodium carbonate stoichiometrically equivalent to the total acidic oxides in the ore and (2) a small quantity of lime, roasting the mixture in the presence of water available to convert the sodium carbonate to sodium hydroxide and at a temperature between 300° and 800° C., and passing into the mixture during the roasting air between four and ten times that required stoichiometrically to satisfy the oxygen demand of the oxygen absorbing oxides in the ore.

12. A process for roasting an ore comprising mixing acidic chrome oxide ore with (1) sodium

carbonate stoichiometrically equivalent to the total acidic oxides in the ore and (2) a small quantity of lime, roasting the mixture in the presence of water available to convert the sodium carbonate to sodium hydroxide and at a temperature between 300° and below about 850° C., and passing into the mixture during the roasting air sufficient to satisfy the oxygen demand of the oxygen absorbing oxides in the ore and less than ten times that required stoichiometrically to satisfy said demand.

CHARLES G. MAIER.

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