ANALYSIS OF SILICATES MATERIALS: A REVIEW

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ABSTRACT

The complete analysis of silicates rocks is a tedious job for an analyst because of difficult decomposition procedure and a number of subsequent separation stages. For the analysis of different major constituents in silicates various classical methods are required: gravimetric, titremetry and spectrophotometry but for the analysis of trace elements the instrumental method is preferable. Methods for the determination of major and minor impurities in silicates rocks, coal and fly ash are generally based on the use of acids or fluxing with an alkaline fusion material. Formerly the use of hydrofluoric acid was carried out to decompose silicate material for the direct determination of silica; later on various fusion materials were used for the complete dissolution of silicate materials. After fusion the fused mass can be dissolved in acid or acid mixtures. In the present study a review of the existing methods, as well as some of the old ones has been carried out.

INTRODUCTION

In earlier times it was the general opinion that minerals and earth have their origin in water, that water is the base of all metals, that rock crystal is formed from purest water and has divine colour and solar heat made it hard. A. B. de Boosdt /1/ and R. Boyle /2/ said that rock crystal is not ice but is a denser product of cold. The ancients knew that fusing sand or rock crystal containing a major amount of silica with salt of potassium or sodium could make glass. J.B. Van Helmont /3/ stated that after fusing such glass could be dissolved in water. J.R. Glauber /4/ called the aqueous solution of the fused alkali and sand "oleum silicum" or "liquor silicum", and J.N. Van Fuchus /5/ called it "wasserglass". The high temperature fusibility and the resistance of silica to chemical reagents have greatly retarded the development of the chemistry of silica. C.W. Scheele's discovery of hydrofluoric acid in 1777 proved a veritable touchstone to the chemistry of silica. J. J. Becher /6/ has identified silica O. Tachenus /7/ stated that silica has acidic properties and shows no tendency to neutralize the acids. T. Bergman /8/ separated silica from siliceous earth by fusing with alkali carbonate and the product was treated with dilute acids. At the beginning of the nineteenth century, G.L.L. de Buffon /9/ and others regarded silica as a primitive earth. A.L. Lavosier /10/ assumed that silica is an oxide of an unknown metal. J.J. Berzelius produced the element by reducing potassium fluorosilicate /K_2 Si F_6/ with potassium and called the product "Kiesel". Silicon does not occur freely in earth – it occurs as silica; silicon dioxide in the form of quartz and it is the next most abundant element in nature after oxygen. It is generally found in all silicate materials. F.W. Clarke's estimate is that it forms 27% of the earth's lithosphere. In quartz it is 12%, felspar 59.5%, hornblende and pyroxene 16.8%and mica contains 3.8%. There are two native forms of crystalline silica, tridymite and cristobalite, which are different from quartz. The non-crystalline hydrated silica is called opal. Silica is also found in animal tissue , in feathers. Human flesh contains 0.08% and 0.15% in the ash /12/ of the skin. Silicon exists in two forms: amorphous and crystalline. Amorphous silica is of two types: one is active amorphous silicon called silicon-$\propto$ and the other passive amorphous silicon forms are silicon-β. The active forms are combustible in air or oxygen, while silicon-β is passive and incombustible. The active forms are insoluble in all acids even in hydrofluoric acid or in a mixture of hydrofluoric acid and nitric acid. But the active forms are soluble in an aqueous solution of potassium hydroxide.

METHODOLOGY

Different authors have adopted various methods for the complete chemical analysis of silicate rocks. Most of the methods are based upon complex ion formation and ion exchange separation. The first step of all chemical analysis is sample decomposition. The process of decomposition varies considerably, from simple extraction with water to the more elaborate technique of fusion. The soluble silicates like clinker and cement are decomposed by hydrochloric acid while the silicates like clay and pozzolanic are insoluble in acid or acids mixtures. Such materials are made soluble by treating with fusion mixture in acid or acid mixtures. The reaction takes place as follows.

$MSiO_3 + 2HCl$ ------ $MCl_2 + H_2SiO_3$ (m-silic Acid)
$2MsiO_3 + Na_2CO_3 + K_2CO_3$ ----2 $MCO_3 + Na_2SiO_3 + K_2SiO_3$
-------------------- ------------------------------
(Insoluble silicate) (Fusion mixture)
$MCO_3 + Na_2SiO_3 + K_2SiO_3 + 6HCL$------ $MCl_2 + 2NaCl + 2KCl + CO_2$
$+2\ H_2SiO_3 + H_2O$
$H_2SiO_3 + H_2O \rightarrow H_4SiO_4 + NH_2O$ ----- H_2SiO_3 in H_2O

where M – silicic acid, O – silicic acid – Polysilicic acid

SiO_{2+} impurities $+4\ HF$---- $SiF_4 + 2H_2O$
$3SiF_4 + 3H_2O$ ---- $H_2SiO_3 + 2\ H_2SiF_6$
$Fe_2(SO_4) + Al_2(SO_4)_3$ --- Heating---- $Fe_2O_3 + Al_2O_3$
$Fe_2O_3 + Al_2O_3 + K_2S_2O_8\ /\ K_2S_2O_8$-----dissolved in water

Most rock analysts prefer to determine Mn, Ti, P, and Fe separately, leaving the silica, and in another step R_2O_3 is determined by precipitating with ammonia; however Cr, V, Zr also precipitate with ammonia when present in more than trace levels, a fact that can introduce error. Hydrofluoric acid has long been used for the decomposition of silicate rocks, usually in combination with perchloric acid, nitric or sulphuric acid. Hoffman /13/ fused rock material with sodium carbonate in a 1:1 ratio and sintered in a platinum dish at 1200°C but this ratio was not sufficient for the decomposition of kyanite, sillimanite or silicate rocks containing large amounts of aluminosilicate. Sodium and potassium hydroxide have been used as externally efficient fluxes for the decomposition of silicate minerals. This decomposition requires a temperature lower than those required for fusion with sodium carbonate. Jeffery and Wilson determined silica and another oxide called R_2O_3 by precipitating with ammonia /14/. Langmyhr and Sveen /15/ and May and Rowe /16/ used hydrofluoric acid without the addition of other mineral acids and applied high temperature and pressure for complete decomposition. Antweiler /17/ used hydrofluoric acid to decompose large fragments of silicate rock by digestion at a temperature of 85° C for 24 hours in a polythene container with a close fitting lid. The use of mineral acids with the hydrofluoric acid is however preferred because it helps to moderate the initial reaction between hydrofluoric acid and finally powered silicate material. The evaporation with a mineral acid additional to hydrofluoric acid also helps to remove the fluoride ion, which interferes in the determination of Al and Ti. Langmyhr /18/ has shown that double evaporation with perchloric acid at a temperature of 180°C reduces the fluoride level to a level that can be leached in a single fuming with sulphuric acid at a temperature of 250°C. Chead and Smith /19/ recommended fusion with ammonium fluoride for the decomposition of beryl and silicate minerals, but sillimanite, kyanite and zircon are not fused with ammonium fluoride. Finn and Klekotka /20/ sintered 0.5 gm of silicate rock material with 0.6 gm of anhydrous sodium carbonate. This method has the advantage of reducing the volume of acid and other reagents that have to be added in the subsequent stages of analysis and of reducing the time necessary or the complete analysis. Rafter and Seelye /21/ recommended that most minerals occurring in the silicates rocks are easily decomposed by sintering with sodium peroxide at temperatures of 480° ±20° C. This evaporation can be done at a temperature of up to 540°C in a platinum crucible without introducing platinum into the rock solution. The sample size should be 240-mesh size but this grinding is not necessary for most silicate rocks, which are readily attacked at 100-mesh size by sintering at the recommended temperature. Borax or a combination of boric oxide or boric acid with sodium carbonate has been suggested by Belcher /22/ for materials rich in alumina and for the decomposition of refractory minerals like corundum, chromium and zirconium containing materials. This combination is used in the decomposition of kyanite, sillimanite and for aluminosoilicate. Biskupsky /23/ has used a flux composed of boric acid and lithium fluoride for the decomposition of silicate rocks and minerals. Methods used for the decomposition of silicates for chemical analyses are usually based on the use of acids or fluxes like sodium carbonate, fusion mixture, etc. Bernas /24/, Langmyhr and Paus /25/ have used a mixture of hydrofluoric acid with other acids to prepare solution of silicate by making use of special Teflon equipment. Alkali fusion has been widely adopted for the analysis of major constituents like silica, alumina and titania and acid dissolution for iron, calcium, alkali elements etc. However, this approach involves complex dissolution techniques and though practicable is not suitable for routine analysis. Recently more emphasis has been projected on the use of lithium metaborate as a flux for decomposing silicate. Ingamells /26/ and James W. Owens /27/ have suggested the use of lithium metaborate which has the advantage of bringing the sample into solution form in one single fusion as lithium and boron are hardly encountered in fly ash materials. Van Loon *et al.* /28/ has given a good account of silicate analysis by lithium metaborate fusion followed by FAAS analysis. ASTM /29/ has also brought out a standard test method for major and minor elements in coal and coke ash based on FAAS using lithium tetraborate. Foder /30/ used hydrofluoric and boric acid mixture for the determination of silica in fly ash. Csondes *et al.* /31/ and Betlinelli *et al.* /32/ have done a comparison study of fly ash sample by different methods. Torigai *et al.* /33/ have determined multi elements in fly ash by microwave digestion using $HClO_4$ /HNO_3 /HF. Swami /34/ have used microwave digestion using HNO_3 / H_2O_2 for the determination of trace elements in Fly ash by ICP-AES. Das /35/ have also used microwave digestion technique for the analysis of multi elements in fly ash by using ICP-MS. N. Singh *et al.* /36/ have used hydrofluoric acid to decompose silicates and silica has been determined quantitatively. The residue remaining after removal of silica has been fused with lithium tetraborate (1: 1 with respect to remaining residue) and subsequent dissolution in dilute nitric. The elements Al, Fe, Ca, Mg, Na, Ti, V, Cr, Mn, Ni, Cu and Zn have been determined by FAAS.

CONCLUSION:

The main shortcoming of the current techniques for the measurement of sulphide ore is that they are expensive and complex in comparison to classical methods. For analysis of silicate ores, especially for major elements, classical gravimetry and titremetry are better in comparison to other instrumental techniques, but for the complete trace analysis the instrumental method is preferable to other methods.

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