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Status of silica in agriculture: A review

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Abstract
Silicon is the second most abundant element in the universe and the second most abundant element on the planet, after oxygen, making about 25 percent of the Earth's crust. Silicon is one of the most useful elements to mankind. Since it exists in the Earth's crust, many plants can accumulate it in large concentrations, in amounts similar to macronutrients. Despite the abundant benefits in agriculture, Si is generally not considered as an essential plant element. In nature, silicon occurs as the oxide (silica) and as silicates, in which it's used in fertilizers. Plant assimilates silicon through roots as silicic acid. Inside plant, it travels to active growing points, where it complexes with an organic compound in the cell walls and make them stronger. The beneficial effects of Si on plants have been demonstrated by many studies using pots, hydroponic, and field experiments. Silicon enhances growth and yield of all annual and vegetable crops, promotes upright growth (stronger and thicker stems, shorter internodes), prevents lodging, promotes favorable exposure of leaves to light, provides resistance to bacterial and fungal diseases and decrease some abiotic stress as temperatures, salinity, heavy metal and Aluminum toxicity. According to science researches, silicon increase plant's resistance to many plant diseases such as powdery mildew and also many insect pests. Silicon has positive effect on the biomass yield under deficit irrigation. Plants subjected to draught, treated with silicon, maintained higher stomatal conductivity, relative water content and water potential. It helps leaves become larger and thicker, thus limiting the loss of water through transpiration and reduces water consumption. Silicon shows great influence on the development of plant roots, thus allowing better root resistance in dry soils and its faster growth.

Keywords: Silicon, silicic acid, determination of silicon etc.

Introduction
Silicon is added to plants as a fertilizer, which can be in liquid or solid state usually applied at the time of planting, but in can be applied at any time during the growing season. Silicon fertilizers in agriculture are still not widespread and they are considered as a modern farm technology, side by side with microbiological fertilizers. Since it's a natural element, silicon based fertilizers can use all farmers, whether they practice integration, conventional or organic farming. Information on the importance of Si in Indian rice farming system is limited (Prakash, 2002) [75]. There is need to identify silicon deficient soils, for determining needed rates of silicon fertilization and for assessing various silicon fertilizer sources. Rice and sugarcane are Silicon (Si) accumulator plants. No other crop requires as high Si as required by rice and sugarcane.

Si plays a significant role in imparting both biotic and abiotic stress resistance and enhances productivity. Si is also the only element known that does not damage plants upon its excess accumulation. High accumulation of Si in rice has been demonstrated to be necessary for healthy growth and high stable production. For this reason, Si has been recognized as an "Agronomically essential element" in Japan and silicate fertilizers have been applied to paddy soils (Ma *et al.*, 2001) [50]. In recent years Si has been regarded as quasi-essential element (Epstein, 1999 and 2005) [19, 20]. Several studies suggest that Si enhances disease resistance in plants, imparts turgidity to the cell walls and has a putative role in mitigating the metal toxicities. It is also suggested that Si plays a crucial role in preventing or minimizing the lodging in the cereal crops, a matter of great importance in terms of agricultural productivity.

Seven international conferences on silicon in agriculture were held at different parts of the world since 1999. As such, many of the plant scientists from India are still unaware of the importance of silicon in agriculture especially as it relates to plant health and soil productivity. In India, though research on silicon has been initiated earlier, the necessity for silicon fertilization to the rice crop has not been widely evaluated as in other countries.

Production of 5 t/ha of grain yield of rice is estimated to remove about 230-470 kg elemental Si from soil, depending upon soil and plant factors. Absorption will be about 108 % more than

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the nitrogen content. Adequate supply of silicon to rice from tillering to elongation stage increases the number of grains per panicle and the percentage of ripening (Korndorfer et al., 2001) [7]. It is also suggested that the silicon plays a crucial role in preventing or minimizing the lodging incidence in the cereal crops, a matter of great importance in terms of agricultural productivity.

There is need to identify the nature and magnitude of the Si status of different rice eco-systems and thereby developing suitable Si management agenda for obtaining or sustaining rice yield potentials of improved rice cultivars. Since yield responses of rice to Si application are related to available Si in soils and the Si content of rice plants, there is a need for evaluation of simple and rapid extractant for determination of available soil Si based on the crop response and its uptake. Several extractants are being employed in different countries for determination of plant available soil Si. Most of them apply an anion to replace adsorbed Si and have been tested by determining the correlations between Si analyzed in the extract and crop yield. Not all of them were intended to extract the complete amount of plant available Si, Hence, there is need for evaluating suitable extractant to determine available soil Si based on the crop uptake.

Acquaye and Tinsley (1965) [1] used citric acid (0.1M) as an extractant in estimation of plant available silicon in soils and this extracts specifically adsorbed silicon apart from water soluble silicon. Similar results were also noticed by Sauer and Burghardt (2000) [79]. Fox et al. (1967) [23] compared several extractants to extract plant available Si from an oxisol of Hawaii. They found an increasing extraction capacity of different extractants in the following order: H_2O ~$CaCl_2$ ~ $Ca(NO_3)_2$ ~ $Ca(OAc)_2$ < $MgSO_4$ < $Ca(H_2PO_4)$ <HOAc. It was noticed that Calcium phosphate extracted the greatest amount of Si in different soils of Hawaii. Fox et al. (1967) [23] and Khalid et al. (1978) [42] used the water as extractant to determine the water soluble silicon fraction in soils. The weakest extractant after water was CaCl2, which only extracts the easily soluble Si fraction (Berthelsen et al. 2001) [7]. Haysom and Chapman, (1975) [29] compared 0.01M CaCl2, 0.5M ammonium acetate, and 0.005 M sulphuric acid for their ability to extract plant available Si from soils and found that silicon extracted by CaCl2 showed the highest correlation to sugarcane yield (r2 = 0.82*). Imaizumi and Yoshida (1958) [33], Ayres (1966) [4] and Wong and Halis (1970) used acetate buffer solutions to extract plant available Si from soils. Snyder (2001) [7] reported an acetic acid extraction, used at soil testing laboratory at the university of Florida everglades research and education center (EREC) as the standard method to analyze plant available Si in soils used for rice farming. Nonaka and Takahashi (1990) [69] reported that acetate extraction was too strong for soils previously fertilized with calcium silicate, because it dissolved a part of non available Si from the fertilizer. Continuous shaking for 16 hours with 0.005M sulphuric acid dissolves specifically adsorbed Si from clay silicate minerals, so that the amount of plant available Si were overestimated (Hurney, 1973) [31].

Nayar et al. (1977) [68] compared N sodium acetate buffer (pH 4.0) with three other chemical extractants (distilled water, 0.2N HCl and 0.025 M citric acid) and it was found that extracting power of different extractants for Si as: 0.2N HCl > 0.025 M citric acid > N acetate buffer > water. Silicon extracted by citric acid showed better correlation with the Si uptake by the rice plants. The phosphate anion was used to extract adsorbed Si from soils to assess plant available Si

(Khalid et al., 1978) [42] in volcanic soils of Hawaii. Kato (1998) [39] reported that in contrast to acetate buffer extraction, phosphate buffer did not overestimate the silicon availability in soils previously fertilized with silicates. Similar results were also noticed by Snyder (2001) [7]. Korndorfer et al. (1999) [44] evaluated four different extractants (0.5M acetic acid, NaOAc (pH 4.0), 0.01 M CaCl2 and distilled water) and found that 0.5M acetic acid gave the best estimate for the available silicon in upland rice soils of Minas Gerais, Brazil. Berthelsen et al. (2001) [7] reported that CaCl2 extracts the easily water soluble Si, and that of acetate, acetic acid and phosphate acetate dissolves some of exchangeable Si, while citric acid and sulphuric acid extracts specifically adsorbed Si. Since the latter two extracts were very acid and longer time of shaking resulted in over estimation of plant available silicon in soils. Kato (1998) [39] reported that the combination method of extraction of silicon by phosphate buffer solution after the incubation under submerged condition was found to be the best method to estimate available silicon in paddy soils of Japan. The silicon extracted by acetic acid was correlated to silicon uptake by rice and rice grain yield in soils of Florida (Snyder, 1991). The chemical method of extraction by using sodium acetate buffer (pH 4.0) was the most widely used extractant in Japan to measure available silicon in paddy soils (Imaizumi and Yoshida, 1958) [33].

The silicon extracted with 0.5 M acetic acid appeared most suitable for evaluating Si availability, followed by extraction with citric acid at 1%. These methods provided the best correlations with rice straw and panicle Si percentage (R2 = 0.899 **, R2 = 0.768 **, and R2 = 0.839 **, R2 = 0.774 ** respectively). These methods, being rapid and effective in extracting Si in comparison to other methods, appear to be the most suitable for routine soil testing for Si in the Everglades Agricultural Area in South Florida. (Filho et al., 2001) [22]. Shigezumi et al. (2002) [83] reported that extraction by using phosphate buffer solution was found to be superior over other methods of extraction of available silicon in soils of Japan. The sodium acetate buffer extracted the greatest amounts of Si (0 to 509 mg kg−1), followed by acetic acid (1 to 239 mg kg−1) and calcium chloride (3 to 109 mg kg−1) in organic and mineral soils of Florida. Acetic acid and sodium acetate buffer soil-test Si values were fairly well correlated (r = 0.77) and both methods performed well across a wide range of soils. Results with calcium chloride were poorly correlated with acetic acid (r = 0.73) and also poorly related to sodium acetate buffer (r = 0.57). After considering only the subset of soils testing at or below the critical value, the correlation (r = 0.84) between acetic acid and sodium acetate buffer extractions was improved (Rodrigues et al., 2003) [11].

Wang et al., (2004) [94] evaluated seven extractants viz., deionized (DI) water, 0.5 M acetic acid, 1 M sodium acetate buffer (pH 4.0), 0.5 M ammonium acetate (pH 4.8), 0.1 M hydrochloric acid, 0.5 M citric acid, and Mehlich -III, to determine plant available silicon in 30 Louisiana soils. The amount of extractable Si resulted from the use of different extractants was in the order of Mehlich III > citric acid > HCl > acetic acid > acetate buffer > NH4OAc > DI water, as determined by colorimetry. Silicon extracted by different extractants was well correlated among citric acid, HCl, acetic acid, acetate buffer, and NH4OAc (R2 = 0.611; P< 0.001). Water and Mehlich III showed poor correlations with other extractants (R2 = 0.430). Extraction techniques for plant-available Si include extractions with water, CaCl2, acetate, acetic acid, phosphate, H2SO3, H2SO4, and citrate. The

extractants show different capabilities to desorb silicic acid, with H2SO3, H2SO4 and citrate having the greater extraction potential (Daniela et al., 2006) [10].

Forms of silicon and status of silicon in soils

Mineral soils develop from rocks or sediments and are mainly composed of primary crystalline silicates such as quartz, feldspars, mica and secondary silicates, especially clay minerals (Iler, 1979 & Conley et al., 2005) [32, 9]. Moreover they contain Si of biogenic origin (Jones, 1969) [36] and pedogenic amorphous silica (Drees et al., 1989) [18]. Silicon also occur in soil as complexes with Fe, Al, heavy metals and organic matter (Farmer et al., 2005) [21] Silicic acid is also dissolved in soil solution with some part of the silicic acid adsorbed to soil minerals, particularly oxides and hydroxides of iron and aluminium (Hansen et al., 1994 & Dietzel, 2002) [28, 16]. Dissolved silicic acid in soil solutions primarily occurs as monomeric or oligomeric silicic acid (Iler, 1979) [32]. Knight and Kinrade (2001) reported that monomeric silicic acid (H_4SiO_4) dissociates into $H+ + H_3SiO_4$ - above pH 9 and into $2H+ + H_2SiO_4^{2-}$ above pH 11. Oligomeric silicic acid is only stable at high concentration of silicic acid at pH >9. In most of soils and natural waters only undissociated monomeric silicic acid occurs (Dietzel, 2000) [15]. The Si compounds in the soils are classified into soil solution and adsorbed Si forms (Monosilicic and polysilicic acids), amorphous forms (phytoliths and silica nodules), poorly crystalline and microcrystalline forms (allophane, immogolite and secondary quartz) and crystalline forms (primary silicates: quartz, feldspars & secondary silicates: clay minerals) (Daniela et al., 2006) [10]. The dissolution of Si in paddy soils is influenced by soil temperature, soil redox potential, soil pH and Si concentration in soil solution (Sumida, 1992) [91]. The average available Si status of eight different soil types of Kerala (South India) as adjudged by four different extractants revealed that Silica extracted by 0.025 M citric acid ranged between 250 to 1500 kg ha-1 with an average of 700 kg ha-1 (Nair and Aiyer, 1968) [64]. Nayar et al. (1982 a) [65] reported that in 5 out of 9 soils (mostly belonging to red and laterite groups) studied, silicon content ranged from 8 to 83 ppm and considered to be highly deficient. Subramanian and Gopalaswamy (1990) [89] reported that the plant available Si status of rice growing soils Kanyakumari, Madurai, Chinnamannur of Tamil Nadu were 29, 70 and 40 ppm, respectively. The plant available soil Si (mean) extracted by N NaOAc (pH 4.0) in soils of Orissa and Andhra Pradesh were 139 and 278 ppm respectively (Nayar et al. (1982a) [65]. However, there is no national database on Si availability in Indian soils although it's available in other countries of the world. It is apparent from the reviewed literature (Prakash, 2002) [75], that most of the paddy soils studied was deficient in Si.

Methods of silica determination from soil

Robinson, 1945 the earliest procedures used to analyze various materials for silicon was based on gravimetric methods, utilizing chemistry that produced either losses or increases in weight. Typical weight loss method utilized HF to evolve silicon as SiF_4 gas. He used this principle to analyze for silicon in soils after first bringing silicon into solution by fusion for determining silicon in an organic matrix such as plant tissues, the organic matter can be removed by oxidation at 550 ºC. After solubilizing non–silicon elements in 6 M HCl, the sample is filtered through ash less paper retains the silicon precipitate. The paper is ignited and weighed. Then HF is used to evolve the silicon so that the weight loss is assumed to be silicon.

Imaizumi and Yoshida, 1958 [33] proposed the use of molar sodium acetate buffer (pH 4.0) for gauging plant available silicon in soils. The buffer is made by diluting 49.2 ml acetic acid, 14.8 g anhydrous sodium acetate to 1 liter and adjusting to pH 4.0 with acetic acid or sodium acetate. Ten gram of air dried soil is placed in a 200 ml flask with 100 ml of the sodium acetate buffer. The flask is placed in a water bath for 5 hours at 40 ºC and shaken "occasionally". After filtering, silicon in the filterate is determined by the silicomolybdate blue method. Kawaguchi and Matsuo, 1958 [40] have proposed another method, in which they evaluated the silica supplying power of soil by simultaneously examining the ratio of the number of atoms of Al, Fe and Si dissolved in 0.2 N HCl extract of the soil. Mc Keague, 1963 [53] was investigated the extraction of water-soluble silicon from soils who found that the concentration of silica in the extracts of shaken sample was larger than if the soil and solution had attained equilibrium by prolonged standing. Mc Keague explained this as being due to abrasion caused by shaking the soils. He found that the amount of silica extracted from soils decreased with increasing pH and decreasing temperature. The successive extraction showed evidence of desorption process. In rapid semi-micro chemical system, the silicon from Na_2CO_3 fusion is dehydrated with $HClO_4$, washed free of metallic cations with 6 N HCl and then is brought into solution in NaOH and determined colorimetrically by the molybdosilicic yellow colour method by Jackson, 1967. Hesse, 1971 [30] the total silica content of a soil is almost invariably measured gravimetrically as silica after fusion or digestion of the soil. One gram of soil is taken into platinum crucible, anhydrous sodium carbonate is mixed and heated in an electric furnace to 1200º C then it is cooled and then digested with 5 M HCl containing little ethanol then acidified by adding about 10 cm^3 of concentrated HCl and 10cm^3 of 60 per cent perchloric acid. Cooled and then diluted with 25 cm^3 warm water, filtered through Whatman No. 41 filter paper and residue is washed with 0.5 M HCl. The combined residue and filter paper are ignited in platinum crucible in muffle furnace. The loss of weight gives total silicon. He also proposed analytical method for water soluble silica in soil. According to him, 1 g of 2 mm soil is weighed to which 50 cm^3 distilled water is added. Shaken for a few minutes, allow to stand overnight. Suspension is filtered through Whatman no. 42 filter paper, 25cm^3 clear filtrate is pipette out, 1 cm^3 of ammonium moly date is added then 1 cm^3 of sulphuric acid is added. It is allowed to stand for 10 minutes and diluted to about 90 cm^3 to which 2 cm^3 of citric acid solution is added and diluted to 100 cm^3. The transmittance is read at 410 nm. Haysom and Chopman, 1975 [29] proposed the use of 0.01 M $CaCl_2$, for extracting plant–available silicon from soils. Two gram soil is shaken for 16 hours with 20 ml extractant in a 50 ml Nalgene tube using an end-over-end shaker. After centrifuging at 2000 rpm for 10 minutes, the supernatant is analyzed for silicon. Khalid and Silva, 1978 [42] used as water extract (3 g soil in 30 ml water and shaken for 4 hours) and a phosphate extract to gauge plant available silicon. In the latter test 3g soil is shaken for 4 hours with 30 ml, 0.1 M acetic acid, containing 50 mg P L^{-1}as Ca (H_2PO_4)$_2$ and adjusted to pH 3.5 with NH_4OH. It was assumed that water extract measured the "intensity factor" and the phosphate buffer measured the "capacity factor". Multiple extractions were employed with later extract.

Nonaka and Takahashi, 1988 [70]; 1990 developed a method for measuring water soluble silicon in rice soil that involves flooded soil incubation. By this method, 10 g air dried soil sample (< 2mm size) is submerged in a 100 ml cylindrical bottle (about 4.5 cm) with 60 ml water and incubated at 40 ºC for a week after which time the supernatant is analyzed for silicon content. Sumida, 1992 [91] considered the 2 weeks period between sampling and reporting the results to be a serious disadvantage of this method for commercial use developed two additional incubation methods. One requires 4 weeks of incubation at 30º C and the other requiring an unstated period of incubation of soil in a series of silicon of varying concentration. Because of the time requirement and complexity of these methods, neither appears suitable for use in a routine soil testing laboratory. Barbosa-Filho et al., 1994 [6] were used extractants like 0.5 M acetic acid (1: 2.5 v/v ratio), citric acid 1 percent (1:10 and 1:25 v/v ratio), distilled water (1:10 and 1:25 v/v ratio), TRIS buffer pH 7.0 (1:10 and 1:25 v/v ratio), incubation method (soil samples incubated with water for 4 weeks at 30 ºC) (1:4 v/v ratio). The concentration of dissolved silicon in soil extracts from all methods is determined colorimetrically using a Technician Autoanalyser.

More et al., 2014 [61] was determined available Si by molybdenum blue method. Extract was prepared by shaking 1g of 2mm sieved soil and 50 ml distilled water. It was kept overnight. 25 ml of this extract was taken to which 15 ml dilute HCl, ammonium moly date, citric acid and sodium sulphite was added. The optical density was measured at 650 nm exactly 1 minute after adding the reluctant.

Silicon in stress
Seebold et al., (2001) [81] have tested the effects of Si on several components of resistance to blast using susceptible, partially resistant and completely resistant rice cultivars. They reported that regardless of cultivar resistance, incubation period was lengthened and the number of sporulating lesions, lesion size, rate of lesion expansion and number of spores per lesion were significantly reduced by Si application. Similar results were also noticed by Onodera, (1917) [72], Maekawa et al. (2001) [51]. Miyake and Takahashi (1983) [58] reported that by increasing the Si concentration in the culture solution, the Si content in the cucumber shoot increased, resulting in a reduced incidence of powdery mildew disease. The Si content of leaves increased proportionally to the increased Si concentration in the culture solution, the incidence of powdery mildew decreased in strawberry (Kanto, 2002) [37]. Silicon deficiency in barley and wheat leads to a poor growth habit and increased powdery mildew susceptibility (Zeyen, 2002) [96]. Datnoff et al. (2005) [12] reported that the occurrence of brown spot, stem rot, sheath brown rot on rice, fusarium wilt and corynespora leaf spot on cucumber and several diseases in Turf grass were decreased significantly by the application of higher levels of Calcium silicate as a source of Si. Liang and Abandonon (2005) [49] reported that application of silicon at varied levels helps in significant reduction of damages caused by various insects, pests and diseases in soils of South Africa. Savant et al. (1997) [80] noticed that application of silicon suppresses insect pests such as stem borer, brown plant hopper, rice green leaf hopper, and white black head plant hopper and non-insect pests such as leaf spider and mites. Similar results were also noticed by Sasamoto (1961) [78] and Sujatha et al. (1987) [90]. Two possible hypothesis for Si enhanced resistance to diseases and

pests have proposed by Cherif et al. (1994) [8]. In the first one, Si deposited on the tissue surface acts as a physical barrier and other one is that Si functions as a signal to induce the production of phytoalexins. Similar results also noticed by Datnoff et al. (2003) [11].

Silicon and abiotic stresses
Takahashi, (1966) reported that Silicon application increases the resistance of rice to radiation stress. The growth recovery of radiation treated plants was much faster with silicon supplied plants compared to that of the plants without Si supply. Water deficiency leads to the closure of stomata and subsequent decrease in the photosynthetic rate. Silicon can alleviate the water stress by decreasing transpiration by forming silicon cuticle double layer. Silicon deposition can reduce the transpiration rate by 30 percent in rice (Ma et al., 2001a) [50]. The effect of silicon was pronounced under water stressed conditions (Low humidity) than rice that cultivated under non stressed conditions (high humidity) (Ma et al., 2001a) [50]. Silicon application in rice is effective in alleviating the damage caused by climatic stress such as typhoons, low temperature and insufficient sunshine during summer season (Ma et al., 2001a) [50]. Agarie et al. (1998) observed that electrolyte leakage caused by high temperature (42.5oC) was less pronounced in the leaves grown with Si than in those grown without Si.

Silicon and Chemical stress
Silicon plays a vital role in alleviating the heavy metal toxicity, nutrient toxicity, nutrient imbalance, salinity and so on. Ma and Takahashi (1990a) [69] noticed that Si supply resulted in a larger increase of the dry weight of rice shoot at a low P level (14 mM) than at a medium level (210 mM). Application of silicon helps in alleviating the adverse effects caused due to the application of excess N fertilizers (Morimiya, 1996) and Ohyama (1985). An alleviative function of Si on Mn toxicity was observed in hydroponically cultured rice (Okuda and Takahashi, 1962), barley (Williams and Valmis, 1957), bean (Horst and Marschner, 1978) and pumpkin (Iwasnki and Matsumura, 1999). Silicon was also effective in alleviating Fe excess toxicity in rice (Okuda and Takahashi, 1962). The beneficial effect of Si under salt stress was observed in rice (Ye et al., 1999), wheat (Ahmad et al., 1992) and barley (Liang et al., 1996). Matoh et al., (1986) reported that shoot and root growth of rice was inhibited by 60 percent in the presence of 100 mM NaCl for three weeks, but Si addition significantly alleviated salt induced injury. Aluminium toxicity is a major factor limiting crop production in acid soils. Ionic Al inhibits root growth and nutrient uptake (Ma et al., 2001b). Alleviate effect of Si on Al toxicity has been observed in sorghum, barley, maize, rice and soyabean (Cocker et al., 1998).

Methods of silicon determination from plant
Piper, 1950 put forth two methods of silica determination in plant i.e. wet ashing and dry ashing methods. Dry ashing refers to processes in which the sample is ignited. The sample may be ignited alone or after moistening with sulphuric acid, in which case a sulphated ash is obtained. It is always carried out at low temperature as possible. It requires considerable experience and patience. As there is possibility of loss of elements, if ashing is carried out at too high temperature, wet ashing is more preferable and convenient than dry ashing method. The most common method of wet ashing includes

digestion of the sample with mixture of sulphuric acid and nitric acids or sulphuric, nitric and perchloric acids. In wet ashing method, oxidation is carried out in solution in acid medium, the temperature can't exceed the boiling point of the mixture used, complex insoluble silicates are not formed and all bases are obtained in solution in the excess of acid. Piper, 1950 was proposed wet digestion with sulphuric, nitric and perchloric acids. On account of rapidity and ease with which this digestion is carried out, the relatively small amounts of reagents used and the non-retention of other substances by the silica, this method of digestion is most valuable for accurate determination of nearly all of the ash constituents. Nayar and Aiyer, 1968a [67] used a method in which oven dry plant samples were digested with tri-acid mixture of nitric acid, sulphuric acid and perchloric acid in the ratio of 10:1:4 and the silica after dehydration was treated with 0.5N hydrochloric acid. This was filtered and the residue washed free of metallic ions with 6N hydrochloric acids. Jackson, 1958 [35]; found that the residue was brought into the solution by treatment with hot water, 5 per cent sodium hydroxide. Murthy *et al.,* 1965 silica determined colometrically by silico molybdate method as modified. Nayar and Aiyer, 1968 [67] also compared several types of extractants and they reported that 0.025 M citric acid gave a closer correlation between the SiO_2 content of plants and the soluble SiO_2 in soils. Su *et al.,* 1983 Silicon in rice straw is typically determined gravimetrically. The remaining precipitate is assumed to be SiO_2 termed "crude silica" which is removed by filtration and weighed.

Nonozamsky *et al.,* 1984 [71] also described a rapid technique for extracting silicon from plant tissue. By their method ground plant material was shaken overnight at room temperature in a solution of HCl and HF and remaining plant debris were removed by filtration. Majumdar *et al.,* 1985 [52], and Snyder *et al.,* 1986 [87] the analytical procedure generally involves oxidation of organic matter and acid dissolution of various components of the straw. Karathanasis and Hajek, 1996 [38] showed several modern techniques have been used to determine the total silicon content of soils, plants and fertilizers without pre analysis solubilization of the matrix. X-ray flourecence spectroscopy (XRFS), which also is known as X-ray emission spectrography or X-ray spectrochemical analysis, assesses the presence and concentration of silicon in soil and plant materials by measuring the characteristics secondary radiation emitted from a sample that has been excited with an X-ray source.

More *et al.,* 2014 [61] determined the total silica from mango leaves by taking 0.1 g oven dried leaf sample which was digested on a hot plate with 5 ml concentrated HNO_3. The digestion was continued till brown fumes ceased and the volume was reduced to about 2 ml which took about 30 minutes. The resultant solution was then transferred with repeated washings into tall stainless steel beakers containing 1 to 1.5 g of AR sodium carbonate in suspension so that there was sufficient alkali in excess after neutralization of the acid. The alkali suspension in the stainless steel beaker was then boiled for 3 to 5 minutes to ensure complete dissolution of silica. The resultant solution after cooling was made up to 250 ml and stored in polythene bottles. The silica was determined by rapid micro-determination method. The silica was converted into molybdenum reactive form with 10 per cent ammonium molybdate solution, which was estimated colorimetrically using ascorbic acid, on spectrophotometer at 660 nm wavelength.

Available silicon content in soils

Kelley and Brown, 1939 [41], Krauskopf, 1959 [47] and Mc Keague and Cline, 1963a [53] reported the soluble silica in the range of 2 to 375 ppm in various soils. Mink, 1962 [57] suggested that silicon removal through excessive irrigation might accelerate evolution of low humic latosols to humic Latosols. However, the level silicon in water extracts of soils was sufficiently low that irrigation even with mountain water containing 2.5 ppm silicon made this unlikely. Fox *et al.,* 1967 [23] were used four extractants for silicon to survey the silicon status of Hawaii soils. The value of water soluble silicon for montmorillonite, Kaolin, Calcite, Kaolinite and allophone varied from 5.2, 8.4, 6.1, 1.7 and 1 to 5.9 ppm, respectively. The general order for extractable silicon from soils developed on basalt and alluvium was: Humic ferruginous latosol < Humic latosol < low humic latosol < Dark magnesium clay. Miller, 1967 [57] observed the silicon content in strongly calcareous Millville clay loam soil moistened with distilled water, extracted after 1 hr., it gives silicon content as 22 ppm and when extracted after air drying it gives value of silicon content as 20 ppm. When slightly acidic sinks clay loam soil moistened with distilled water, extracted after 1 hr, it gives value of silicon content as 21 ppm and when exctracted after air-drying it gives 16 ppm silicon. Gascho, 1976 [25] studied the silicon status of Florida Sugarcane, he observed the water soluble silicon in highly organic soil of Everglades in the range of 0 to 95 mg kg^{-1}. Nayar *et al.,* 1977 [68] observed on an average, Kerala soils contained about 700 kg of citric acid soluble (available) silica per ha. Available silica (SiO_2) was determined by four extractants from lateritic soil of Kerala. It was as follows: water soluble 17 to 34 ppm, 0.2 N HCl soluble 38 to 419 ppm, sodium acetate soluble 43 to 179 ppm and 0.025 M citric acid soluble 43 to 281 ppm with mean values of 24, 252, 79 and 125 ppm, respectively. Hallmark and Wilding, 1982 [26] showed the concentration of silicon in soil solution appear to be controlled by dynamic processes. Consequently kinetics may be the controlling factor for maintaining soluble silicon levels in solution. Douglas *et al.,* 1984 [17] found that level of soluble silicon in Palouse area soils were at least three times greater than values reported by Mc Keague and Cline. Mc Keague and Cline, 1963a also found that silicon movement in the surface soil of an acidified Walla silt loam was higher than at more line lower profile depth. Murthy and Ponnamperuma, 1986 [62] noticed that silicic acid-$Si(OH)_4$ concentration in wetland rice soils of Philippines extracted by water and citrate-bicarbonate-dithionite (CBD) reagent range from 3.7 to 16 ppm and 187 to 887 ppm, respectively. The concentration of $Si(OH)_4$ extracted by water and CBD was found to decrease with increase in pH and the amount of silicic acid extracted by CBD was 13 to 150 times of those extracted by water. Anilakumar *et al.,* 1990 [2] a field experiment conducted in a well-drained lateritic sandy loan soil of Regional Agricultural Research Station, Pattambi, Kerala. They inferred that the silicon content in soil at 13, 23, 33, 44, 54, 65, 75 days after transplanting. The values were 150.9, 122.9, 115.5, 110.5, 133.9, 150.5 and 147.7 ppm, respectively. Barbosa-filho *et al.,* 1994 [6] analyzed soil for silicon determination using extractants *viz*, 0.5 M acetic acid, citric acid 1per cent, distilled water; TRIS buffer (pH 7.0, supernatant method, incubation method and batch method. According to him, value of distilled water extractable soil silicon was in the range of 4 to 20 mg lit^{-1} Si. Liang *et al.,* 1994 conducted an experiment to study the silicon supplying

power of 23 paddy soils. They found that the available silicon content of the surveyed soil ranged from 151to387 SiO_2 mg kg^{-1} with a mean value of 237 mg kg^{-1} SiO_2.

Dhamapurkar, 1999 [14] studied that the water soluble (SiO_2) silica content in typical laterirtic soil at Dapoli was 22 kg ha^{-1}. Korndorfer et al., 2000 [46] working on wet land rice and 28 field experiments conducted in the Everglades Agricultural area, they observed that the soil silicon content varied from 4 to 85 mg dm^3 within the locations. Mongia and Chhabra, 2000 [60] studied profile samples of alluvial alkali soils of Indo-Gangetic plain from three prominent sites viz., Central Soil Salinity Research Institute (CSSRI) and Gudda experimental farm, Karnal farm (Zarifa Viran Series) and Dilip Nagar experimental farm, Kanpur, UP. (Dilip Nagar series). Unreclaimed and reclaimed alkali soils from the above three locations had water soluble silicon content in the range of 295 to 384 and 192 to 317, 3550 to 525 and 101 to 389 and 243 to 444 and 287 to 454 mg kg^{-1} respectively. Selvakumari et al., 2000 conducted a field experiment in alluvial soil of Tamil Nadu Agricultural University farm (TNAU) Coimbatore. The sodium acetate (NaOAc) extractable silicon at pH 4.0 found to be 82 mg kg^{-1}. Snyder, 2001 was established silicon soil test range of low (< 7 Si mg lit^{-1}.medium (7.24 Si mg lit^{-1}) and high (>24 Si mg lit^{-1}). Mongia et al., 2003 marked buffer extractable silicon at 0 to 15 cm and 15 to 30 cm depth of reclaimed alkali soil was 11.3 and 13.9 mg per 100 g soil, respectively.

Total silicon content in soils
In Hawaii, interest in soil silicon goes back to the end of the last century when Maxwell, quoted by Moir, 1936 called attention to the low level of total soil silica. The mean of 1300 soil samples, was about 28%. Ayres, 1943 [3] studied clay soils of Hawaii belonging to three distinct great soil groups, the humic, hydrol humic and aluminous humic ferruginous latosols but they all had low total silicon and high total Al contents (7% and 12%), low base saturation and correspondingly low pH respectively. Bair, 1966 [5] and Gascho and Andries, 1974 [24] observed many Histosols in the Everglades contain 1 to 2 total Si dag kg^{-1} (Si per cent) or less. Fox et al., 1967 [23] surveyed soils of Hawaii for silicon determination. Total silicon content of soil with Montmorillonite, Kaolinite, Calcite, Goethite-Gibbsite-Illite and Allophone minerals varied from 19.5, 12.5, 13.8, 1.2, 7.6, 5.0 and 8.1 to 13.6 per cent, respectively. Lechler et al., 1981 [48] reported thee total silicon in the list of 12 reference mineral soils from the south eastern USA ranged from 20 to 44dag kg^{-1}. In three years continuous study (1981 to 1983) in northeastern Everglades, Snyder et al., 1986 [84] observed total soil silicon 0.98, 0.81, 0.70 dag kg^{-1}. Phonde, 1987 [73] studied lateritic soils from VRL zone at Dapoli, Wakavali, Awashi, Shiragaon, Lanja and Phondaghat locations. Total SiO_2 content at these locations varied from 45.78 to 49.12, 43.14 to 50.28, 47.52 to 53.96, 40.41 to 55.71, 40.39 to 45.78 and 57.07 to 58.64, respectively, with mean value of 48.98 per cent. They also studied total silica content in medium black soils from VRN zone at Dahanu, Palghar, Karjat. Pargaon (Panvel), Roha and Repoli (Mangaon). The values were in the range of 52.66 to 53.42, 52.09 to 63.39, 52.33 to 58.42, 57.24 to 57.44, 45.72 to 51.32 and 57.28 to 59.30, respectively, with mean value of 55.90 per cent of above these locations.

Conclusion
The different reviews showed that the application of the silicon to the rice crop give beneficial effects in crop production and also overcome the biotic and abiotic stresses. The role of silicon not only work as an essential nutrient but also as a beneficial nutrient was unnoticed because of its natural abundance. But if the application of more nitrogen was done then the crops become more succulent, prone to lodging and increased the incidence of pest and diseases which can be overcome by the application of silicon by which soil could be sustain. The plant available Si in soil is an important soil-related factor which may be closely associated with progressive yield declines experienced in Konkan. To the period of the issue of Si nutrition in rice production remains largely unknown. Identifying and implementing strategic Si nutrition management strategies may very well play a critical role for reversing deteriorating yield trend. Si has been shown to affect the availability of phosphorus in the soil. There should be development and standardization of different sources of silicon and quantify the amount of different sources for the rice crop.

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