

## PHYSIOCHEMICAL TRANSFORMATION OF WASTE OF SUPER PHOSPHATE INDUSTRY INTO NEW GENERATION SILICATE FERTILIZER AND ITS USES FOR RICE GROWTH UNDER SALINE ENVIRONMENT

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### Abstract

Rice (*Oryza Sativa* L.) is a major staple food of majority of people in different countries of the world. Rice is highly susceptible to salinity and its yield is severely limited under salt stress environment. However, one favourable character of rice is that it is a silicate accumulator plant. We investigated the effect of new generation Si (silicate) fertilizer (produced from the waste of the phosphate industry, which mainly consisted of amorphous silica, potassium hydroxide, pulverized coal and aluminium chloride) amendments on two contrasting rice varieties. The produced smart Si fertilizer materials were solidified, dried, granulated and calcined to remove toxic compounds and to enhance end product's solubility. Two rice varieties IRRI-9 (coarse rice) and Basmatti-2000 (fine rice) were grown under saline environment. Twenty six days old uniform sized rice seedlings were transferred in glazed clay pots filled with non-saline ( $EC_e = 1.66 \text{ dS m}^{-1}$ ) and saline soil (induced  $EC_e = 6 \text{ dS m}^{-1}$ ) under flooded conditions. New generation Si-fertilizer was used @ 0, 75 and 150 mg Si  $\text{kg}^{-1}$  soil. Plants were grown until maturity stage and different physiochemical parameters were investigated. Both, biological and paddy yields of rice were reduced significantly ( $p < 0.05$ ) due to induced salt stress; however less reduction was observed in coarse as par to fine rice variety. The Si fertilizer amendment in growth environment significantly ( $p < 0.01$ ) enhanced plant dry biomass (4-folds) with reference to control treatment and similarly paddy produce of rice was also enhanced (3-folds) in both plant culture environments. Sodium concentrations in plant shoots were negatively correlated ( $r = -0.90, p < 0.01$ ) with shoot dry matter, but potassium concentrations depicted positive correlation ( $r = 0.90, p < 0.01$ ) in rice plants. Induced Na concentration was significantly reduced in plants receiving Si in the growth medium. Shoot Si concentration was significantly correlated with shoot potassium uptake ( $r = 0.66, p < 0.05$ ) and insignificantly with shoot Na uptake ( $r = 0.23, p < 0.05$ ). Applied silicate fertilizer in the root environment significantly enhanced K to Na ratio in rice genotypes exposed to salinity however, impact on K: Na ratio was insignificant in normal soil. Increased selective K uptake and reduced Na uptake or translocation may be one of the possible strategies of induced salinity tolerance by silicate nutrition in rice.

**Keywords:** Si-fertilizer, Coarse and fine rice, Salinity and K: Na ratio

### Introduction

Soil salinity is a global issue in terms of plant growth in irrigated agricultural areas under arid and semi-arid climatic zones of the world. Approximately, 6.3 m ha of cultivated lands are deteriorated due to varying degrees of salinity/sodicity in Pakistan (Gafoor *et al.*, 2004). Crop adaptation to salinized soil is crucial to sustain agriculture in Pakistan where there is a less chance to gain new land because good lands are already under intense cultivation to feed the highly exploding population demand. Several chemical amendments for salt affected soils, biological improvement in salt tolerance of crops and physical as well as engineering approaches are already in use for crop production on such problematic soils. However, it is still highly imperative to find out/redesign environment friendly tool for economic plant production under saline soils, to ensure food sustainability in countries of emerging economies with limited resources (Qureshi & Barrett-Lennard, 1998). Among all these approaches, mineral nutrient fertilization in rooting environment has gained a considerable interest to combat the negative effects of salt stress (Raza *et al.*, 2006). Exogenous K nutrition mitigated adverse effects of soil salinity in wheat crop (Akram *et al.*, 2007), Ca in bean plants (Awada *et al.*, 1995), and N in *Phaseolus vulgaris* (Wagenet *et al.*, 1983). In addition, some quasi-essential but highly beneficial plant nutrients also ameliorate adverse effects of soil salinity such as Si-

nutrition that is still deemed to be improved plant growth and yield under salt free and saline environment (Agurie *et al.*, 1992; Devirm *et al.*, 2016). However, numerous studies around the globe proved that Si fertilization had highly positive effects on plant growth under biotic and abiotic stresses (Rodrigues *et al.*, 2003; Ma, 2004). These positive effects are usually more evident in Si accumulator plants. In general, plants of Gramineae family are Si accumulator (Matichenkov & Kosobrukhov, 2004) and rice is an important member of this family.

Rice is a salt susceptible, important food crop for more than half of the global population. Its fine variety (Basmatti-salt sensitive) is grown in Pakistan. This variety has high demand throughout the world due to its unique aroma. However, its per hectare yield is lesser compared to short-statured (coarse-salt tolerant) rice variety. Lianghe & Michael (2000) reported that salinity adversely affected yield of rice in river deltas and former floodplains, particularly in semiarid and arid climates and losses of rice yield were 40% at soil  $EC_e = 3 \text{ dS m}^{-1}$ . Rice plants accumulate Si in their shoot (0.1 to 6%) based on dry weight (Gong *et al.*, 2003). Higher the Si accumulation in plant shoots more is the tolerance against salt stress in rice.

In Pakistan, farming community rely on superphosphate for P nutrition, which is mostly manufactured from local rock phosphate (Hazara rock phosphate). Phosphate rock mineralogy can be highly variable, depending primarily on the origin, its formational or post depositional history and the

type and degree of near surface processes that the rock has been subjected to. The main constituents of Pakistan rock phosphate are apatite minerals along with high amount of non-phosphatic accessory minerals (Si-enriched). After acidulation of rock phosphate for superphosphate manufacturing, silicate remains as a liquid by product and dumped as residual waste at disposal sites. These disposal sites are almost half century old and are a serious environmental concern for soil and air pollution. Silicate fertilizers have highly beneficial effects on plants to combat different stresses such as salinity. Several possible mechanisms are suggested by different investigators emphasizing that Si nutrition may induce tolerance in higher plants against salinity stress. These mechanisms include, Si improved water balance under salt stress environment (Romero *et al.*, 2006), enhanced photosynthesis and ultrastructure component of leaf (Shu & Liu, 2001), enhancement of antioxidant activity (Zhu *et al.*, 2004) and reduction of sodium toxicity (Liang *et al.*, 2003).

In present study, keeping in view the importance of silicon nutrition for higher crops growth under different stress condition, this Si-enriched waste of P industry was processed as a new generation Si fertilizer by an innovative approach and its subsequent use for the healthy growth of rice under normal and saline conditions. This new generation Si fertilizers developed by slurry formulation, solidification, drying, granulation and purification processes was assessed.

## Materials and Methods

**Physicochemical characteristics of experimental soil and culture conditions:** A bulk of (0-15 cm from surface) of a sandy clay loam soil, classified as Hyperthermic Ustalfic Haplargids (Gee & Bauder 1986) was sampled from Sargodha University Research Farms. A sample was collected from the bulk soil dried in air, ground finely and sieved with a 2 mm size sieve. Analysis of soil samples was carried out to estimate different physical and chemical characteristics (Table 1). Saturated soil paste was prepared and soil pH was measured by using calomel glass electrode (Beckman pH meter). Soluble salts ( $EC_e$ ) of the saturated extract were measured by EC meter (WTW- Cond 3I 5i). The  $CaCO_3$  in soil samples were estimated by a method of acid dissolution (Loepfert & Sunrez 1996). Total and available Si contents by acetate buffer method (Rodriguez *et al.*, 2003) and organic matter was measured by Walkely-Balack protocol (Nelson & Sommers 1982). Glazed pots of clay origin (each of 10 kg capacity) were filled with soil. Salinity was artificially developed in half pots with different salt combinations to obtain soil  $EC_e$  level up to 6 dS m<sup>-1</sup> and the remaining pots served as control pots (original soil  $EC_e$  of 1.16 dS m<sup>-1</sup>). This  $EC_e$  level was used because earlier researchers documented that rice plants showed almost 50% reduction in yield at 6 dS m<sup>-1</sup> EC level. Basal doses of primary nutrients were added at the recommended rates. Silicon was applied along with three different levels 0, 75 and 150 mg Si kg<sup>-1</sup> soil using new generation silicate fertilizers. The soil was mixed thoroughly and distilled water was applied to maintain 70% field capacity. Temperature of the greenhouse varied in between 35 to 45°C. Relative humidity varied from 27 to 30% during day and night

duration, respectively. Light intensity ranged from 600 to 1600  $\mu\text{mol photon m}^{-2} \text{s}^{-1}$  relying upon day and weather pattern during growing season of rice crop.

**Table 1. Selected physicochemical properties of soil used in experiment.**

Property	Unit	Values
Sand	(%)	55.16
Silt	(%)	24.19
Clay	(%)	20.65
Textural class	-	Sandy clay loam
Soil paste pH	-	7.68
$EC_e$	dS m <sup>-1</sup>	1.16
Organic matter	(%)	0.78
Calcium carbonate	(%)	2.01
$NaHCO_3$ -P	(mg kg <sup>-1</sup> )	6.05
Available K	(mg kg <sup>-1</sup> )	220
Available Si	(mg kg <sup>-1</sup> )	31
Total Si	(mg kg <sup>-1</sup> )	225

**Plant material:** Certified seeds of two contrasting rice varieties were collected from Kala Shah Kakoo Rice Research Station, Pakistan. These were (a) 'IRRI-9'-intermediate growth duration, salt tolerant, short-statured coarse genotype originated from Philippines and, (b) 'Basmati-2000'-fine rice with unique aroma, salt sensitive, of Pakistan origin. For the pre-germination, soaking of both rice varieties were carried out with demineralized water for 48 hours prior to sowing. Sowing of pre-germinated seeds was done in pre-washed river bed sand present in iron trays lined with polyethylene sheets. Distilled water was applied to sand medium for germination purpose. Twenty six days old uniform sized rice seedlings were transplanted in pots filled with saturated soil. Mature rice plants were harvested and grains were separated from shoots. The collected plant samples were kept in an oven with forced air mode at 65°C for 48 hrs. Oven dried plant samples were meshed into a mill to screen through a 1 mm sieve. Digestion of 0.2 grams powder was performed in 2 ml  $H_2O_2$  (50%) and 6 ml NaOH (50%) for 4 hrs at 150°C. Estimation of Si was done from the digested samples by Amino-molybdate Blue Method using spectrophotometry (UV-visible spectrophotometer- Shimadzu, Spectronic-100, Japan) at wave length of 650 nm (Elliot & Snyder 1991). Sodium and potassium concentration in meshed rice shoots was estimated by flame photometry.

**Statistical analysis:** Silicate and salinity treatments were imposed factorially in a 3×2 Randomized Complete Block Design replicated thrice. MStat-C statics program was used for data analysis. Means of rice genotypes, salinity and silicon were compared by using DMR test (Steel *et al.*, 1996).

## Results

**Plant measurements:** Rice genotypes exposed to saline soil ( $EC_e = 6 \text{ dS m}^{-1}$ ) showed statistically ( $p < 0.05$ ) significant reduction in shoot dry matter (SDM) of plants reference to normal ( $EC_e = 1.16 \text{ dS m}^{-1}$ ) soil environment (Table 2). However, reduction in shoot biomass was less

in IRRI-9 compared to Basmatti-2000. Sodium stress affected shoot biomass yield up to 2.6-fold in coarse and 3-fold in fine rice. New generation silicate fertilizer addition in root zone significantly ( $p < 0.01$ ) improved shoot biomass (53% & 48%) at medium level of Si and an increase (140% & 170%) at high level of Si (150 mg Si Kg<sup>-1</sup> soil) was observed respectively among both rice varieties grown under salt stress. The SDM accumulation was higher due to Si application in Basmatti-2000 when grown in normal soil, but a reverse trend was observed in case of plants exposed to saline soil.

The induced salinity reduced the paddy yield of both rice genotypes significantly. Silicate amendment in culture medium enhanced the paddy yield significantly ( $p < 0.05$ ) of rice varieties both under untreated (normal) and treated (saline) soil conditions. Both varieties showed significant differences in paddy yield production as IRRI-9 yielded more paddy (2.10, 6.80 g/pot) compared to Basmatti-2000 (2, 6.70 g/pot), respectively under saline and normal soil conditions.

Silicate amendments enhanced the paddy yield significantly ( $p < 0.05$ ) (4.10 g/pot) at medium level and 5.20 g/pot at high level of Si application in case of coarse

variety of rice. The paddy yield of fine rice was increased relatively from 112.34 to 261% at medium and high level of Si replicates under salt stress.

**Mineral contents:** Addition of new generation silicate fertilizer in growth environment altered ionic contents of rice straw due to sodium toxicity (Table 3). Higher Na concentration (1.70%) was observed in Basmatti-2000 when grown in Si deprived saline soil environment. Lower Na concentration (0.35%) was noted in IRRI-9 when exposed to silicate replicated at salt free culture environment with maximum level of Si (150 mg Si kg<sup>-1</sup> soil). Contrarily, highest potassium (1.72%) concentration was estimated in coarse rice shoot with Si applied soil condition free from salt but lowest K concentration (0.35%) was noted under Si deprived saline soil environment. Silicon content varies with the change of Si supply in culture medium. Basmatti-2000 responded better to exogenous Si application as compared to IRRI-9. The Si amendment had strong influence on the K: Na ratio in all culture environments (Table 3).

**Table 2. Effect of Si application on straw and paddy yield of rice genotypes grown in normal and saline soil.**

Si application rate (mg kg <sup>-1</sup> of soil)	IRRI-9	S.B-2000	IRRI-9	S.B-2000
	Normal soil (1.16 dS m <sup>-1</sup> )		Saline soil (6 dS m <sup>-1</sup> )	
	<b>Straw yield (g/pot)</b>			
0	20.60 ± 2.97 c	18.19 ± 2.67 cd	7.90 ± 0.99 e	6.13 ± 0.65 ef
75	27.60 ± 3.77 b	25 ± 3.53 b	12.03 ± 1.71 d	9.9 ± 1.12 d
150	33.83 ± 4.87 a	31.33 ± 4.78 ab	14.30 ± 2.92 c	12.83 ± 2.54c
	<b>Paddy yield (g/pot)</b>			
0	20.60 ± 2.97 c	18.19 ± 2.67 cd	7.90 ± 0.99 e	6.13 ± 0.65 ef
75	27.60 ± 3.77 b	25 ± 3.53 b	12.03 ± 1.71 d	9.9 ± 1.12 d
150	33.83 ± 4.87 a	31.33 ± 4.78 ab	14.30 ± 2.92 c	12.83 ± 2.54c
0	6.30 ± 1.76 c	6 ± 1.54 cd	2.10 ± 0.19 d	2 ± 0.13 d
75	9.40 ± 2.21 bc	7.80 ± 2.01 c	4.20 ± 0.88 c	4 ± 0.80 cd
150	12.40 ± 2.13 a	10.60 ± 2.33 b	6.80 ± 1.97 c	6.70 ± 1.88 c

S.B = Supper basmati; ± = Mean values with standard error

**Table 3. Effect of Si application on ionic composition of rice straw grown in normal and saline soil.**

Si application rate (mg Si kg <sup>-1</sup> soil)	IRRI-9	S.B-2000	IRRI-9	S.B-2000
	Normal soil E. C 1.16 dS m <sup>-1</sup>		Saline soil E. C 6 dS m <sup>-1</sup>	
	<b>Na conc. (%)</b>			
0	0.44 ± 0.06 d	0.47 ± 0.06 d	1.69 ± 0.16 a	1.77 ± 0.19 a
75	0.39 ± 0.06 d	0.40 ± 0.06 d	1.12 ± 0.10 b	1.19 ± 0.11 b
150	0.35 ± 0.06 d	0.36 ± 0.06 d	0.65 ± 0.08 c	0.68 ± 0.08 c
	<b>K conc. (%)</b>			
0	1.4 ± 0.16a	1.53 ± 0.17 a	0.35 ± 0.05 d	0.36 ± 0.05 d
75	1.65 ± 0.17 a	1.69 ± 0.17 a	0.52 ± 0.07 c	0.55 ± 0.07 c
150	1.75 ± 0.18 a	1.75 ± 0.18 a	1.11 ± 0.10 b	1.31 ± 0.11 b
	<b>Si conc. (%)</b>			
0	2.03 ± 0.19 c	2.50 ± 0.23 c	2.60 ± 0.21 c	3.10 ± 0.31 bc
75	3.50 ± 0.31 b	4.10 ± 0.37 b	4.10 ± 0.30 b	4.10 ± 0.37 b
150	5.06 ± 0.61 ab	5.10 ± 0.67 a	5.20 ± 0.62 a	5.20 ± 0.78 a
	<b>K: Na ratio</b>			
0	3.18 ± 0.16 b	3.25 ± 0.17 c	0.21 ± 0.03 f	0.20 ± 0.03 f
75	4.23 ± 0.37 b	4.22 ± 0.33 b	0.46 ± 0.06 e	0.46 ± 0.06 e
150	5 ± 0.51 a	4.86 ± 0.41 a	1.71 ± 0.17 d	1.93 ± 0.18 d

S.B = Supper basmati; ± = Mean values with standard error

## Discussion

Soil salinization is a worldwide issue in irrigated agriculture. Rice is a salt sensitive plant and salinity modifies physiological and biochemical character of rice crop and significantly reduces various growth stages of plants subjected to salt stress (Mass & Hoffman, 1977). Potassium–silicon interaction proved to enhance growth of land plants particularly under different environmental stresses (Epstein, 1999). Different possible strategies that enhance plant tolerance against salt stress due to silicate application have been proposed (Mukkram *et al.*, 2011). The present experiment was an attempt to make a new generation active silicate fertilizer from industry waste and to estimate its beneficial impact on the growth and salinity tolerance of two contrasting rice varieties. Active silicate application in growth medium significantly improved dry biomass and grain production in rice when grown in normal as well as saline soils. More biomass accumulation under salt stress conditions showed beneficial effects due to introduction of silicate in growth environment which was in lines with the findings of Al-aghabary *et al.*, (2004) and Mukkram *et al.*, (2010) who observed beneficial impact of Si application on chlorophyll quantity, and antioxidative enzyme system of tomato and wheat plants grown under salt stress environment. Ahmad *et al.*, (1992) also reported more dry mass production by Si inclusion in saline environments than in non-saline environment.

Correlation matrix between different parameters indicated that shoot Na concentrations were significantly negatively correlated ( $r = -0.90, p < 0.01$ ) with SDM, while K-concentrations statistically significant and positively correlated ( $r = 0.90, p < 0.01$ ) of coarse and fine rice leaf (Fig. 1). Silicon concentrations in plants are directly proportional with SDM of rice plants grown under both salt free and saline soils, however, this effect is more pronounced in plants those grown under salt stress environment (Fig. 2). The NGSF (New Generation Silicate Fertilizer) application in the growth environment significantly enhanced potassium to sodium ratio in rice specifically salt stress condition but noted non-significant impact of K: Na ratio in normal soil (Fig. 3). Percent reductions of Na concentrations and percent increase in K concentrations in plants grown under normal and saline environment are represented in Fig. 4-5. Percent increase in salinity induced Na concentration was significantly reduced in those plants that were exposed to Si in the rooting environment. Shoot Si concentration depicted significant correlations with shoot potassium uptake ( $r = 0.66, p < 0.05$ ) and statistically non-significant with sodium uptake in shoots ( $r = 0.23, p < 0.05$ ).

Among major salinity tolerance mechanisms due to Si application is an increased K uptake (Liang *et al.*, 1999). Liang *et al.*, (2005) also documented that potassium uptake increased and sodium uptake was decreased significantly under saline environment that might be a major tolerance strategy in higher plants when Si was included in the growth medium. Present results also showed substantial increase in potassium uptake in both rice varieties under saline conditions when silicon was included in the rooting environment. The fine rice (Basmatti, 2000) showed better response to the exogenous Si application than coarse rice (IRRI-9). The applied Si also improved K: Na ratio in saline (treated) as well as in normal (untreated) soil conditions. The maximum K: Na ratio was observed in plants exposed to high level of exogenous Si applied under both control and saline soil environment. This highlights a possible mechanism/strategy of Si mediated enhanced tolerance of rice plant against salinity.

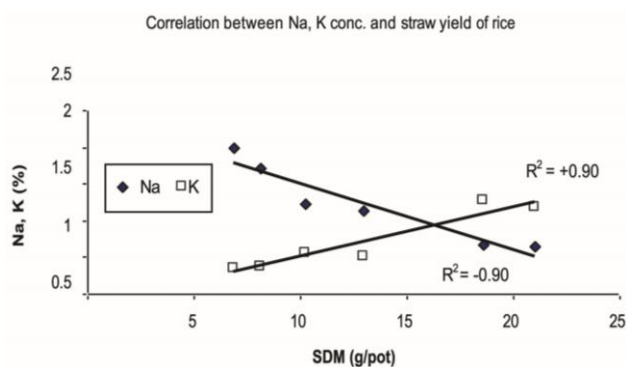


Fig. 1. Relationship between Na, K conc. and straw yield of rice exposed to saline soil.

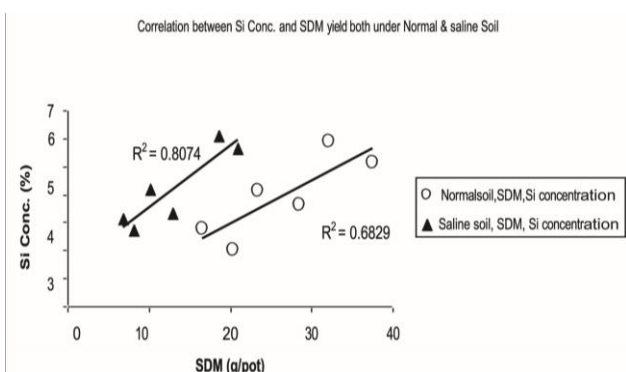


Fig. 2. Correlation between Si concentration and shoot dry matter (SDM) yield both under normal and saline soil root environment.

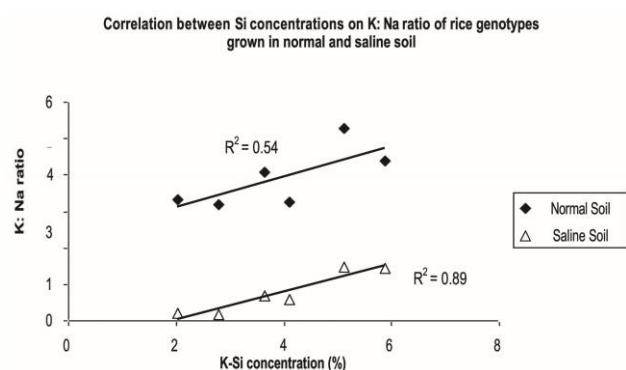


Fig. 3. Correlation between Si-concentration on K:Na ratio of rice plants grown in normal and saline soils.

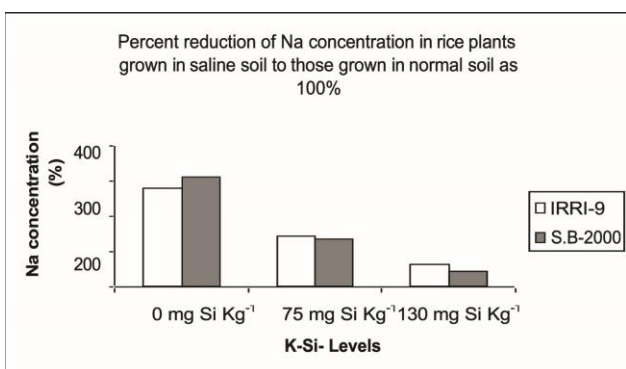


Fig. 4. Percent reduction of Na concentrations in rice shoot grown in saline soil to those grown in normal soils.

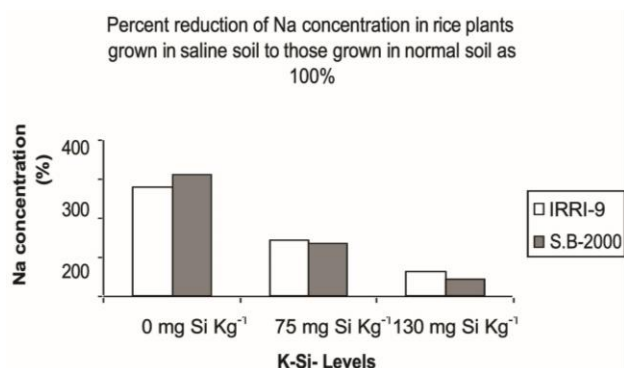


Fig. 5. Percent increase in K concentration of rice plants grown in saline soil to those grown in normal soils.

## Conclusion

The chemical transformation of raw silica a waste product of super phosphate industry was achieved by a unique approach. After all processes, the raw silicate is converted into a new generation silicate fertilizer. Silicate fertilizer can be successfully used in the production of rice plant both under normal and salt stress growth environment. The possible mechanism to induce the salinity tolerance in rice by silicate is reduction of Na uptake and enhancement of selective K uptake. This study proved that active silicate use can help a lot to ensure food security in arid climate especially to Si accumulating field crops such as rice.

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