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Strategy on Utilization of Glauconite Mineral as Source of Potassium

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Preface

As early as 1939, Arnon and Stout laid down the criteria defining the concept of 'essential nutrients' for plants. According to them an element to become qualified as essential, it must: (i) be involved in completion of the life cycle of the plants; (ii) not be replaceable by another constituent and (iii) be directly involved in plant metabolism. Today we know, out of some 110 known elements, 17 are classified essential. Potassium (K) is one among these vital substances, which is indispensable for growth, development and yield of a broad spectrum of plants. It is an accepted fact that arable crops need K in amounts, which are equal to or second only to another essential nutrient - nitrogen (N). In case, K supply is sub-optimal, crop growth, produce, quality and productivity get adversely affected.

When India became independent, agricultural scientists supposed that Indian soils were well supplied with K and supplementation with fertilizers was unnecessary. But the need for K fertility management became acute, once response to the Green Revolution (GR) technologies of mid 1960s started waning in intensity and extent. Subsequent farmers' field research univocally established that the extant degree of K deficiency in Indian soils was far more widespread than believed earlier. Not only that, the creeping sickness due to weakening K status of soils was expanding at a faster pace also. The emerging scenario spurred the need for K-fertilizers for sustaining productivity growth and maintaining market-preferred quality of produce, specifically of horticultural, vegetables and plantation crops. Since Indian agriculture depends entirely on imported potash, the burgeoning demand for K entails fattening burden on foreign exchange; nearly US $ 1500 M/year.

With the above background, on September 13, 2016, NAAS organized a Consultation Meet on this important issue under the convenership of Prof J.C. Katyal, Former Vice-Chancellor, CCS Haryana Agricultural University, Hisar. The main goal of the discussions of this Meet focused on examining the potential of indigenously available K-bearing mineral glauconite as a substitute to imported potash fertilizers. Incidentally, India abounds in this ore embedded in the greensand found in Rajasthan, Madhya Pradesh, Uttar Pradesh and Gujarat. Glauconite has also a proven agronomic record both as K source and soil amendment for several field crops cultivated across diverse agro-eco regions. Besides, amenability to open quarrying and minimal treatment before field use make glauconite economically favorable also. The other aim of the Meet was to give fillip to GOI's flagship 'Make in India' Program.

It is NAAS's abiding belief that the policy options along with action plan presented in this publication will be of immense value while addressing emerging concerns on declining rates of productivity growth of field crops due to mounting incidence of K deficiency in Indian soils. The Academy appreciates the efforts of Prof J.C. Katyal in convening and steering the deliberations of this important Consultation Meet. It also compliments the contribution of all distinguished participants, and resource persons. The editorial support extended by Drs K.K. Vass and V.K. Bhatia is acknowledged.

(Panjab Singh)
President

Strategy on Utilization of Glauconite Mineral as Source of Potassium

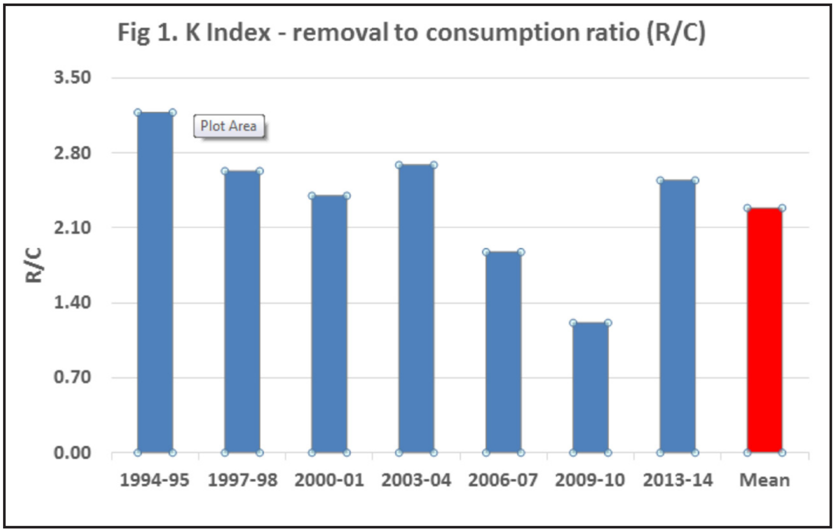
1. BACKGROUND

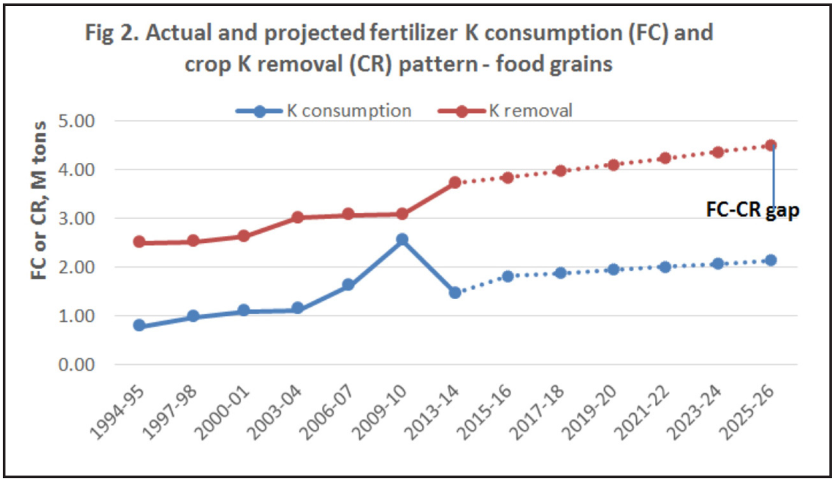
1.1 Criticality of potassium (K) in sustainable growth of agriculture

Seventeen nutrient elements are essential for growth and development of all crop plants. K is one among these vital substances and is un-substitutable by anyone else. Crops need K in amounts, which are equal to or second only to another essential nutrient - nitrogen (N). If its supply is sub-optimal, crop productivity falls because healthy yield enhancing features like shape, colour, size, taste and number and weight of grains or fruits get adversely affected. This happens because K is involved in activation of growth related enzymes, photosynthesis, water balance, energy regulation and protein synthesis. K has a strong influence on efficient use of water by plants. Its deficiency in soils upsets water uptake via roots and disturbs its loss through the stomata. It is known to play a vital role in pacifying drought vulnerability of crops. K deficiency increases disease vulnerability and suppresses response to fertilizers, particularly N fertilizers. Above all, K plays a crucial role in maintaining consumer-preferred quality of grains, fruits, vegetables, spices, condiments, tea, coffee, coconuts.

1.2 State of K in Indian soils and crops

After independence, it was widely believed that Indian soils are well supplied with K. Soil scientists and agronomists, who led the soil fertility management of food grain crops, propounded this thesis. With time, turning a Nelson's eye to potash treatment led to deficiency, which with time emerged as a creeping sickness of soils and crops. Need for K fertility management was felt, once response to the Green Revolution (GR) technologies, particularly treatment with fertilizers started waning in intensity and extent. Back to back cropping combined with high productivity increased mining of soil K reserves, amplifying thereby deficiency syndrome. Although fertilizer potash consumption grew significantly (CAGR @5.4%since 1970-71), it was hardly adequate to neutralize the escalating liquidation of soil K reserves. Rising mean K index to the unacceptable range of 2.2 (removal/addition ratio) during the last 20 years is an evidence to that development (Fig 1). Over the last 2 decades, estimates on potash removal - based merely on 30% of the total crop uptake needing replenishment (assumption: 70% K removed is being contributed by soil, crop residues turnover and irrigation water) - by food grain crops and addition through fertilizers (assumption: 70% of the total potash consumption diverted for food grain crops) showed a deficit of ~1.5 M tons/annum. It is projected to grow at the rate of 2.5 M tons by 2025 (Fig. 2).





Primary data source for Figs 1 and 2: FAI (2015)

Since incessant negative balance aggrandizes depletion of soil reserves, by and by K deficiency intensified in soils and crops. In the process, the soils that earlier were medium in K-availability turned low and those that were high in availability declined to medium category (Sekhon, 1999). Developing K deficiency is among the key factors contributing to regression in productivity growth of food grains from 3.1% before 1990 to 2.1% thereafter.

Progressive findings from long-term fertilizer experiments and soil testing, established widening incidence of cross-country K deficiency. Presently, at least 50% of the Indian soils spread over 200 districts suffer from K insufficiency in varying degrees (Table 1). Soils of sparsely vegetated arid regions, intensively farmed areas and poorly buffered acid soils exhibit K deficit, which is quite significant than other regions and soil types.

Table 1. K deficiency in soils – Categories and Extent (Rao et al., undated)

K status		**Deficiency category**	**No. of districts**
Exchangeable K	*Non-exchangeable K*		
Low	Low	Severe; K application must	15
Low	Medium	Critical; K application essential	18
Low	High	Necessary; K application helpful to arable crops	2
Medium	Low	Necessary; K application helpful to horticultural crops	58
Medium	Medium	Necessary; K application helpful to high-intensity cropping	115
Overall: 50% of cultivated soils (acid, aeolian and intensively cultivated alluvial soils); spread across ~200 districts; K treatment needed			

Accordingly, crops of these farming zones and K-loving horticultural (classically banana and pineapple), vegetable (normally potato and sugar beet) and cash crops (e.g., cotton, sugarcane, oilseeds...), in particular, require higher K applications (Table 2).

Table 2. K removal/ton of main produce by diverse crops

Crop	**K removal (kg)/ton**
Wheat	32
Sunflower	126
Potatoes	6.2
Carrot	6.2
Banana	20.3
Coconut	12.0
Black pepper	3.3
Coffee	174

Data from several sources

Further plantation crops (coconut, areca nut, oil palm, cashew, tea, coffee, rubber...) and spices/condiments are faced with double whammy of having big hunger for K and their being concentrated in K deficient acid soils. In order to improve quality and productivity of these crops, irrefutably K management strategies need to be exceptionally aggressive. Otherwise, ignorance cost of not applying potash (return on investment) to field crops alone will range from Rs 1000 to Rs 2000/ha (IPNI South Asia Program Data); being lot higher for K requiring horticultural and plantation crops.

With surging K deficiency in Indian soils and shifting emphasis on cultivating K demanding, nutritionally dense and export earning crops, the time is ripe to pay more attention to K that has historically been neglected. India will have to substantially raise K application levels from the current 17 kg K_2O/ha to at least 30 kg K_2O/ha. Since imports fill our entire demand for K, it means current foreign exchange burden of ~US $ 1500 M/annum is likely to inflate/deflate in future, depending significantly upon the price movement. It, therefore, is of urgent necessity to harness indigenously available potash mineral resources to contain the import bill.

Taking into cognizance, the serious emerging issue of K-deficiency in Indian soils a National level Consultation Meet was organized by NAAS on September 13, 2016, under the convenership of Prof J.C.Katyal. The main goal of the discussions was to present a graphic account of the indigenously available K-bearing mineral glauconite (an iron potassium silicate; K_2O content 5-8%) as a substitute to imported potash. Glauconite was preferred over the other two potash-bearing minerals (polyhalite and sylvite) found in India because of amenability to low cost open quarrying and proven agronomic benefits as K source in its native form. The other aim of this Consultation was to give fillip to GOI's flagship 'Make in India' Program. Incidentally, commercially viable industrial processes for manufacturing K fertilizers from glauconite through beneficiation are available.

2. GLAUCONITE

2.1 Origin

Glauconite owes its origin to sedimentary marine deposits. It is generally thought to have formed in shallow marine seas near the interface of land and water. It, therefore, lies on the top of lithosphere with little or no overburden. Glauconite – an iron-potassium-silicate is embedded in what is called 'greensand rock'. Its content in greensand is a good measure of the exploitable quality of the rock. Chemically, it is described as $[(K, Na)(Fe^{+3}, Al, Mg)_2(Si, Al)_4O_{10}(OH)_2]$. It contains ~5 to 8.5% K_2O (PS. GOI Minerals Book 2016 indicates existence of some glauconites in India with K content as high as 11% K_2O).Besides K, it is a rich source of Si (~50%), Fe (~16%), Mg(~2 %) (all expressed in oxide forms), and some 30 trace elements of which zinc, copper, molybdenum are the most important. Some glauconites are also rich in calcium and phosphorus.

Glauconite discharges K gently and slowly into soil solution. Thus, it saves plants from usual root injury associated with concentrated and fast acting water soluble muriate of potash. Gradual release also shields K from leaching and possible groundwater pollution. This trait is of special significance in acid soils, which because of dominating positive charge are specifically vulnerable to repel a cation like K (K^+). Glauconite, therefore, is admirably safe for soils and plants and overall ecosystem health and is also a more efficient K source. Additionally, long-lasting K release pattern matches very well with K loving perennial crops, which need maintenance of supply over extended periods of time. However, if deficiency is severe and crop need is immediate, fortification with readily available sources or beneficiation to improve content of water soluble K becomes necessary. Further, cross-country information on agronomic performance of glauconite can be found on internet-sites for India: www.tifac.org.in/offer/tlbo/rep/TMS160.htm; Denmark:www.mdi.dk/agroline.htm; USA:http://minerals.usgs.gov/minerals/pbs/commodity/ potash; Brazil: dusolo.com/.../eagle-star-minerals-corp-applies-for-new-phosphate-and-potash-claims and CIS (Formerly Russia): www. glaukos.ru/site/index/articles/?id=5.

From soil physical-chemistry point of view, glauconite is a clay mineral and is a variety of illite. In characteristics, it falls between montmorillonite and muscovite. Its non-expandable nature does not offer interlayer adsorption sites. Resultantly, its K weathers faster than that of feldspar – a high K bearing mineral. Despite being non-stretchy, inherently glauconite is endowed with high cation- or base-exchange capacity; ranging from 20 to 30 centi-moles/kg. This quality prevents downward nutrient flow by strengthening a soil's storability of exchangeable NH_4^+, K^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}...; tightening grip also minimizes leaching loss and groundwater pollution. Because of base/cation stashing power, glauconite is widely deployed to soften hard water – a common practice in the USA.

Unlike most other clay minerals, glauconite exists in sand sized particles (0.02 to 0.05 mm), which are green in colour. Despite bulky mass, glauconite does not behave like sand. Its structure is saturated with hundreds of micro-pores. These tiny apertures play a vital role by contributing to unique water holding capacity; 10 times more than the ordinary sand. This virtue also binds sand particles and enhances their water storage-ability. On the other hand, being non-expandable, glauconite treatment opposes sticking together of clay particles; allowing thereby better aeration and free drainage of expanding clay soils. Improvement in chemical and physical properties indirectly stimulate soil biology and help increasing efficient use of other nutrients. Armed with complex physical and chemical features, glauconite qualifies both as a fertilizer and a soil conditioner. India has known reserves of unexploited 1900 M tons of glauconite. These primarily occur in the States of

Rajasthan, Madhya Pradesh, Uttar Pradesh and Gujarat. Because of lack of clear utilization policy (led by its non-inclusion along with minor minerals listed in the 'Mineral Concession Rules 1960 and 2016' contained in the 'Mines and Mineral Development Regulation Act 1957'), the glauconite mines currently lie commercially unexploited.

All available information points out that glauconite has been used as K source and for soil amendment since the 18th century in the USA (www.garden.com). Almost 100 years later, it was overwhelmed by the availability of high K content sylvite mineral (~52% K) for manufacture of potassic fertilizers. World War 2, however, disrupted potash fertilizer trade and revived the interest in glauconite treatment of acid soils, typically in Europe. In the 1980s, India, then having no indigenously known standard potash deposits (>10% K_2O) for manufacturing fertilizers, put lot of energy and money into glauconite mining. This effort did not reach a logical end, since at that point in time; exploiting potential of glauconite was waylaid by the availability of relatively low priced imported potash. In 2001, TIFAC (Technology, Information, Forecasting and Assessment Council) noted that proposal on enhancing induction of glauconite as a potash source is worth considering. Its launch would not only lead to saving of foreign exchange, but also enable harnessing the utility of unexploited Indian mineral resource. More recently in 2014, Ministry of Mines GOI (Indian Minerals Year Book 2013: Potash) stated that glauconite has potential for direct application to soils in a pro-environment manner. In support, it stated that the glauconite "mixes homogeneously with the soil and provides potash as nutrient for plants. It also increases soil fertility and improves soil texture, porosity and permeability due to more or less uniform grain size". In line with this commentary, it is significant to note that in the USA, glauconite, perhaps, is the only certified organic source of potash anywhere in the world (www.garden.com). The earliest experimental evidence on acid soils proved that certain samples of glauconite performed as good a soluble potash, while some others were inferior (Brant, 1929).This dissertation went on to prove that performance of diverse origin glauconites may not be uniform. It is also expected to vary across test crops and soils. Cited from TIFAC, in India, BCKVV and BHU got encouraging results on direct application of glauconitic sand of UP (http://tifac.org.in/index.php?option=com_content&view=article &id=729&Itemid =205 4/). K release from glauconite was influenced by the particle size and accordingly dry matter yield and K uptake increased as the coarseness of the mineral matter decreased (Srinivas Rao and Subba Rao, 1999).

2.2 Agronomic performance of glauconite *vis a vis* other K bearing minerals

Glauconite is not the only potash mineral that has been evaluated as an alternative to widely-employed K fertilizers. Potash rich feldspars containing up to 13% K_2O and occurring in far greater abundance in the lithosphere is not of much agronomic value. Exceedingly slow release of clawed K in the interlayer positions contributes to its poor performance. In other mica minerals like biotite or its scrap, K is part of the silicate structure and hence not readily available. However, inoculation with potash solubilising micro-organisms and acid treatment are known to enhance their value as K source. Glauconite, because of inherent ability to additionally work as soil ameliorant, outstands other potash minerals for direct application.

2.3 Scope of beneficiation of glauconite

On all counts, glauconite seems to be a superior choice for direct application to acid soils and more specifically for crops requiring slow release K carriers. Examples of such crops, have been detailed in an earlier section. In order to widen scope of glauconite application for early K requiring short duration crops, it has been either fortified with water soluble resources, or beneficiated by heat or acid treatment or both. Power of appropriate bio-inoculants has also been utilized to accelerate release of locked K.

In the pursuit to develop K fortified glauconite products, the mineral is enriched by blending it with a complex of soluble potassic carriers and other nutrient sources. Chinese have patented (CN101575231A) a 'glauconite multi-element compound potash fertilizer'(proportion in parts: glauconite 45-50, potassium chloride/sulphate 6.3-7.6, mono-amino phosphate 1.7-3.6, carbon ammonia 1.7-3.6, urea 34-35). In small field plot tests, the compound potash fertilizer out-yielded a comparable product, but without glauconite (https://www.google.com/patents/ CN101575231A?cl=en).

2.4 Beneficiation

It refers to the process that removes gangue minerals (materials of little commercial value) from an ore to synthesize a high grade or concentrated nutrient source. With glauconite, preparation of beneficiated products follows 3 different routes. First method is removal of iron by applying magnetic force for increasing K concentration of glauconite. Led possibly by treatment simplicity, TIFAC prefers this method of beneficiation for Indian minerals. It, however, suffers from a severe limitation, which relates to the quantum of improvement in the K content of the upgrade product. In absolute terms, it works out to merely 1 percentage point elevation in K concentration. Second procedure of the ore processing centres on acid extraction. A proprietary 'K-Max process' developed by Potash West NL Australia is available for commercial exploitation. It employs a concentrated hot acid leach that breaks down the glauconite, recovering all the K within the mineral in 6 to 8 hours. The process combines well with the open pit quarrying operations, which makes it economically more attractive (http://investingnews.com/company-profiles/potash-west-glauconite-australia/). In India, a chlorodizing-roasting of ore followed by acid leaching has been developed to extract K (http://www.sciencedirect.com/science/article/pii/030175169400041W). Compared to the industrial process of Potash West NL Australia, the commercial potential of the Indian procedure has yet to be established. A Brazilian path adopts 2-step procedure: reacting greensand with an acid industrial effluent and subjecting the product to thermal processing using $CaCl_2$ as a fluxing agent. The third route to upgrade K availability exploits the power of K mineralizing micro-organisms (KMMs). It is done by inoculating glauconite with appropriate microbes. KMMs increase glauconite-K availability due to acids produced during mineralization process. Alternatively, composting of plant and animal residues is done by enriching it with glauconite. Once again, organic acids generated during organic matter breakdown hasten release of glauconite-K.

3. HIGHLIGHTS OF PRESENTATIONS MADE AT CONSULTATION MEET

The main outcome of thematic lectures is summed up as follows:

3.1 Compared to yesteryears, current extent of K deficiency in Indian soils is far more widespread and is expanding; need for potassic fertilizers is on the rise to sustain productivity growth and maintain market-preferred quality of produce, specifically of horticultural, vegetables and plantation crops; burgeoning demand for K entails fattening burden on foreign exchange, since currently Indian agriculture depends totally on imported potassic fertilizers.

3.2 Need for substituting foreign-origin potassic fertilizers with indigenous sources and resources is of far more consequence now than ever before; reviving interest in the indigenously available, but forgotten, K bearing glauconite mineral comes to the fore; favourable economic and environmental considerations justify preference for glauconite compared to other minerals.

3.3 Information on agronomic worth of Indian glauconites as source of K nutrition and soil conditioner is sketchy and superficial; in particular, there is no scientific evidence on suitability of this slow releasing K carrier for perennial crops and the soil conditions under which these crops are cultivated

3.4 Known value of glauconite as soil conditioner has seldom been investigated in India

3.5 Forced by the mining policy inadequacies (non-inclusion of glauconite in the schedule of minor minerals as listed in the Mineral Concession Rules 1960/2016), Indian glauconites lie, poorly explored and commercially unexploited either by fortification or beneficiation

4. THEME AREAS

Based on the deliberations in the Consultation Meet, following themes were identified to formulate recommendations and way forward.

- Current state of glauconite mining with focus on physico-chemical properties of diverse Indian glauconites
- Niche areas, crops and management practices supporting use of native glauconites as K source and soil conditioner
- Potential of K solubilizing (mineralizing) micro-organisms in enhancing the agronomic value of glauconite as direct source of K
- Choice of fortification procedures on blending sparingly soluble glauconite with soluble nutrient sources in balancing the near and long-term K needs of annuals and perennials. Exploitation of industrial beneficiation route for preparing K dense soluble fertilizers

5. THEME-WISE RECOMMENDATIONS:

5.1 Current state of glauconite mining

- Map out distribution of high intensity contiguous deposits of greensand rock to assess availability and more importantly exploitability with favourable economics but without adverse influence on the environmental services.
- Establish bench-mark sites for launching exploration of quality glauconite to be based on the proportion of glauconite in the greensand rock and content of K in the glauconite. Rocks having > 80% glauconite with minimum K content of 5% and more should be the early centres of future development.
- Detailed physico-chemical analysis of exploitable glauconites to establish their potential as source of K and as ameliorant of soil bio-physical properties. Typical focus of this research need to be on understanding the 'intensity' (represented by water-soluble and exchangeable K) and 'quantity' (represented by non-exchangeable K but having potential to enter soil solution) of K release form glauconites of diverse origin. Factors influencing K release processes (particle size reduction and management practices) will be additional objects of glauconite characterization studies.
- Greensand rock, selected as source of glauconite, is likely to contain gangue minerals constituted of pollutant elements. Since their entry into soil and water is seen to pose a challenge to human and livestock health, an assessment on the incidental additions of such harmful elements need to be invigilated on regular basis.
- Government need to declare glauconite in the schedule of minor minerals, since it is not included in the list of Associated Minerals [Chapter XI of Mineral Concession

Rules 2016 of the Mines and Minerals (Development and Regulation) Act, 1957)]. In the meantime, GOI may consider declaring glauconite (and other potash bearing minerals) through a policy instrument as experimental research mines. This will allow leasing to be done at the State level without going through the process of E-Auction. In the long-run, however, it will be necessary to set up a coordination committee of the Secretaries of the Ministry of Minerals and Mines, Ministry of Agriculture and Farmers Welfare and Department of Agricultural Research and Education for the purpose of removing policy distortions and issuing a suitable notification in this regard. It was suggested that Ministry of Agriculture and Farmers Welfare may act as the coordinating agency.

5.2 Niche areas, crops and management practices.

- Identify and prioritize crops and soils likely to be most responsive to the direct application of glauconite as source of K.
- Besides assessing potential of glauconite as source of K, equally important it would be to launch studies on assessing its ameliorative influence on soil physical conditions (structure, aeration…) and water-holding/transmission characteristics.
- Identify management practices – method of application like broadcast versus placement with and without particle size reduction, influence of fortification with soluble sources, inoculation with K solubilizing micro-organisms and enrichment of organic sources during composting.

5.3 Potential of K solubilizing (mineralizing) micro-organisms

- Initiate studies with the aim of isolation and identification of micro-organisms that are efficient K solubilizers and colonizers of glauconite as well. Strengthen these investigations by follow up research on quantifying improvement in the availability of glauconite-K by employing thus identified bacteria, fungi and actinomycetes, alone or as a consortium.
- Explore value of enrichment of organic residues with glauconite before composting with or without inoculation with K solubilizing micro-organisms
- Assess potential use of glauconite as carrier of bio-inoculants, since it is inert, cheap, has excellent moisture absorption capacity, is free flowing and above all is a good source of K and several other essential nutrients.

5.4 Choice of fortification procedures by blending

- Begin investigations on enhancing early K availability to young crops by fortifying glauconite with soluble K sources (e.g., muriate of potash). Include enrichment with other nutrient fertilizers for preparing custom-made carriers suiting site-specific fertility management. In order to synthesize non-segregating mixtures of glauconite and other fertilizers, dry granulation by compaction was recommended for adoption. In terms of economics, compaction equipment is less expensive and easy to install, run and maintain compared to requisite investments on machinery, operative costs and infrastructure for installing alternative wet granulation procedure. Above all, simplicity of dry granulation offers a vast possibility to be turned into a village based industry for synthesizing custom-made fertilizers suiting diverse crops and soils.

- Iron removal from glauconite by magnetic force and use of this K enriched ore for preparing bulk blends with other soluble nutrient carriers was the alternative route suggested for preparing site-specific bulk blends. Likely saving on spiking-proportion of muriate of potash is the stated advantage of this alternative pathway of manufacturing mixed fertilizers.

5.5 Exploitation of industrial beneficiation routes

- On the methods of beneficiation, group recommended to make a feasibility study on commercial suitability of the proprietary 'K-Max process' developed by the Potash West NL Australia (http://investingnews.com/company-profiles/potash-west-glauconiteaustralia/) or any other commercially proven process. However, primary focus of beneficiation should be on glauconites having K content of around 10%. Ore from Sidhi, Madhya Pradesh falls in this class. It can be a joint study involving scientists from the CSIR-Advanced Material and Processes Research Institute Bhopal (originally Regional Research Laboratory), CSIR-Central Institute of Mining and Fuel Research (CIMFR), Roorkee, Fertilizer Association of India, New Delhi and ICAR-Indian Institute of Soil Science (IISS), Bhopal. ICAR-IISS is proposed to also work as Group Convener.

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Note: *The designations and affiliations of the participants are as on the date of Consultation Meet.*