UNIVERSIDADE FEDERAL DE LAVRAS

LUCAS ALBERTH RIBEIRO DO VALLE

AVALIAÇÃO DO POTENCIAL DE USO AGRÍCOLA DA FLUORITA COM ÓXIDO DE SILÍCIO (AgroSiCa), DERIVADO DA FABRICAÇÃO DE FERTILIZANTES FOSFATADOS

LAVRAS – MG

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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Recursos Ambientais e Uso da Terra, para a obtenção do título de Doutor.

Orientador

Prof. Dr. Luiz Roberto Guimarães Guilherme

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APROVADA em 18 de abril de 2016.

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RESUMO

Solos de clima tropical são conhecidos por apresentarem alta capacidade de fixação de fósforo e saturação por alumínio, bem como baixos teores de cálcio e bases trocáveis, portanto a aplicação de fertilizantes fosfatados é uma prática indispensável para a adequada produção agrícola neste tipo de solo. Muitas rochas utilizadas na produção de fertilizantes fosfatados apresentam a fluorapatita na sua composição, quando estas rochas são atacadas com ácido sulfúrico ou fosfórico para produção desses fertilizantes, o ácido hexafluorossilícico (H_2SiF_6) é gerado como um subproduto. Enquanto muitas tecnologias de tratamento têm sido propostas para a remoção do flúor em plantas industriais, pouca atenção tem sido dada ao processo de neutralização do H_2SiF_6 com óxido de cálcio a fim de se obter um produto com grande potencial de uso agrícola, dando um uso inovador e sustentável para o H_2SiF_6. Este estudo avaliou os efeitos da aplicação de um subproduto da produção de fertilizantes fosfatados (fluorita com óxido de silício, daqui em diante denominado AgroSiCa) sobre os atributos químicos do solo, bem como sobre o crescimento das culturas da soja e do milho. Experimentos foram conduzidos em casa de vegetação na Universidade Federal de Lavras (UFLA), Lavras-MG, utilizando diferentes tipos de solos de regiões tropicais e diferentes doses do AgroSiCa. A aplicação do AgroSiCa resultou em um ligeiro aumento do pH do solo e em aumentos significativos nos teores de cálcio, fósforo e silício na solução do solo e na parte aérea do milho e soja. Baixos níveis de flúor foram encontrados nos lixiviados do solo. Houve uma redução significativa dos teores de alumínio lábil. Em suma, o AgroSiCa melhorou as propriedades do solo e contribuiu para um melhor crescimento de ambas culturas. Os resultados mostram que a reação de H_2SiF_6 derivado da produção fertilizantes fosfatados com óxido de cálcio leva a produção de um subproduto com grande potencial para utilização agrícola, especialmente quando aplicado em solos altamente intemperizados. Além de fornecer cálcio e silício para as plantas, a aplicação do AgroSiCa em solos com elevada capacidade de fixação de fosfato e alta saturação de alumínio proporciona vantagens adicionais, uma vez que o fluoreto e o silício desempenharam um papel importante na melhoria das condições destes solos, devido à diminuição da fitoxicidade do alumínio (pois há a formação de formas menos tóxicas as plantas) e da fixação de fósforo, melhorando o desenvolvimento das raízes das plantas e aumentando a eficiência da adubação fosfatada.

Palavras-chave: Subproduto. Indústria de fertilizantes fosfatados. Solos tropicais. AgroSiCa.

ABSTRACT

Phosphate fertilizers are critical for crop production in tropical soils, which are known for having high phosphate-fixing capacity and aluminium saturation, as well as low pH and calcium contents. Fluorine is a component of many phosphate rocks used to make phosphate fertilizers, via a process that generates hexafluorosilicic acid (H_2SiF_6). While many treatment technologies have been proposed for removal of fluorine in industrial facilities, little attention has been given to a process of neutralizing H_2SiF_6 with calcium oxide aiming to find out an alternative and sustainable use of a by-product with a great potential for beneficial use in tropical agriculture. This study evaluated the effect of a by-product of phosphoric acid production (fluorite with silicon oxide, hereafter called AgroSiCa) in levels of phosphorus (P), calcium (Ca), silicon (Si), aluminum (Al) and fluorine (F) and some others parameters in soils as on growth of soybean and corn. Experiments were conducted in a greenhouse condition at the Federal University of Lavras (UFLA), Lavras, Minas Gerais, using different types of soils in tropical regions and different doses of AgroSiCa. The application of AgroSiCa resulted in a slight increase in soil pH and significant increases in calcium, phosphorus and silicon in the soil solution and the shoots of corn and soybeans. We also found very low levels of fluoride in all soil leachates. A significant reduction of labile aluminum levels found in all soils after the cultivation of corn and soybeans. In sum, AgroSiCa improved soil properties and contributed to better growth of both cultures. In sum, AgroSiCa improved soil properties and contributed to a better growth of both crops. Our results show that reacting H_2SiF_6 derived from the wet-process phosphoric acid production with calcium oxide leads to a by-product with potential for agricultural use, especially when applied in highly-weathered soils. Besides providing calcium and silicon to plants, the use of such by-product in soils with high phosphate-fixing capacity and high aluminium saturation delivers additional benefits, since fluoride and silicon can play an important role in improving soil conditions due to the formation of less plant-toxic forms of aluminium, as well as upon decreasing phosphate fixation, thus improving root development and making fertilizer-derived phosphate more available for plant growth.

Keywords: By-product. Phosphate fertilizer industry. Tropical soils. AgroSiCa.

SUMÁRIO

PRIMEIRA PARTE

1 INTRODUÇÃO GERAL

Solos tropicais geralmente são solos muito intemperizados e conhecidos por apresentarem baixos teores de fósforo e de bases trocáveis, elevada saturação por alumínio, baixos valores de pH e elevada capacidade de fixação de fósforo. Estas características reduzem muito seu potencial produtivo, de modo que a aplicação de fertilizantes fosfatados, assim como a calagem, se tornam práticas indispensáveis para uma adequada produção agrícola nestes solos. Com isso, grandes quantidades de fertilizantes fosfatados são produzidas e aplicadas em solos brasileiros, sendo que mais de 30 milhões de toneladas de fertilizantes foram entregues ao consumidor final no ano de 2015 (ASSOCIAÇÃO NACIONAL PARA DIFUSÃO DE ADUBOS - ANDA, 2016).

No entanto, as rochas utilizadas como matéria-prima para a fabricação de fertilizantes fosfatados apresentam em sua constituição cerca de 1 a 4 % de flúor (F) (CRONIN et al., 2000). Quando estas rochas são processadas com ácido sulfúrico ou fosfórico para a produção dos fertilizantes fosfatados, o ácido hexafluorosilícico (H_2SiF_6) é gerado como um subproduto. Este ácido pode ser comercializado para as indústrias químicas, de siderurgia, de metalurgia ou pode ser usado para a fluoretação das águas, no entanto as quantidades produzidas do H_2SiF_6 pelas indústrias de fertilizantes fosfatados são muito maiores do que as quantidades comercializadas deste subproduto. Nota-se que existe atualmente um grande desafio para se buscar destinação adequada para o grande volume do subproduto (H_2SiF_6) gerado nos processos de acidulação de rocha fosfática. Várias tecnologias de tratamento, com base em precipitação, permuta iônica, eletrólise, membrana de osmose reversa, e processos de adsorção foram propostos e testados para a remoção do flúor de plantas industriais (ISLAM; PATEL, 2007), sendo a precipitação o tratamento mais comum (SAHA, 1993). No entanto, estas tecnologias têm sido descartadas pelo alto custo de execução ou pela baixa qualidade e valor do produto final obtido.

Portanto a neutralização do H_2SiF_6 com óxido de cálcio (cal virgem - CaO) a fim de se obter um subproduto (aqui denominado, AgroSiCa) com grande potencial de uso agrícola em solos tropicais, pode ser uma alternativa inovadora e sustentável para a destinação de tal ácido, uma vez que o AgroSiCa contém Cálcio (Ca), Fósforo (P), Silício (Si) e Flúor (F). O Ca e P são nutrientes exigidos em grandes quantidades pelas culturas, o Si é um elemento considerado benéfico à grande maioria dos vegetais superiores, pois confere maior resistência ao ataque de pragas (insetos), nematóides e doenças, diminui a taxa de transpiração e, confere maior eficiência fotossintética (BROADLEY et al., 2012 ; KORNDOFER; GRISOTO; VENDRAMIM, 2011; MARSCHNER, 1995). O F apesar de não ser considerado nutriente de plantas, pode contribuir para melhoria das condições agrícolas de solos tropicais pela redução da fitoxicidade do Al (formação de pares iônicos-Al-F que são formas menos tóxicas as culturas). Além do mais, o F, assim como o Si, pode competir com P pelos sítios de sorção no solo diminuindo sua fixação, aumentando a disponibilidade do nutriente para as plantas e a eficiência da adubação fosfatada, contribuindo para o uso racional das fontes de fósforo que são finitas e não renováveis (CHILDERS, et al., 2011). Contudo, são raros os estudos sobre os efeitos do F nas características químicas de solos de regiões tropicais, assim como no Brasil.

Este estudo propõe a neutralização do ácido hexafluorosilícico com óxido de cálcio para a produção da fluorita com óxido de silício (AgroSiCa), um subproduto com grande potencial de uso agrícola, principalmente em solos tropicais, dando uso alternativo, sustentável e inovador para o H_2SiF_6 gerado nas indústrias de fertilizantes fosfatados, e estuda os efeitos da aplicação do AgroSiCa nas características químicas de solos tropicais e no crescimento das culturas de milho e soja.

2 REFERENCIAL TEÓRICO

2.1 Processamento e obtenção de subproduto da indústria de fertilizante fosfatado com potencial de uso agrícola

As rochas fosfáticas, usadas para extração de fósforo, apresentam em sua composição, minerais pertencentes ao grupo das apatitas, encontrados nas rochas ígneas, metamórficas e sedimentares. As variedades mais comuns que geralmente ocorrem nas rochas de origem ígnea, principalmente em carbonatitos, são a fluorapatita, a hidroxiapatita e, mais raramente, a cloroapatita. Na maioria dos depósitos sedimentares predominam as variedades de carbonatoapatita e carbonato-fluorapatita (francolita) (LAPIDO-LOUREIRO; MELAMED, 2009; McCLELLAN; KAUWENBERG, 1990; ZAPATA; ROY, 2004).

A apatita, especialmente a fluorapatita, usada como matéria-prima para produção de ácido fosfórico, ao ser atacada por “ácido sulfúrico + água”, produz como subproduto da reação, o sulfato de cálcio e ácido fluorídrico, conforme reação geral descrita abaixo (reação 1).

(1) $Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4.2H_2O + 6H_3PO_4 + 2HF$

Observa-se pela composição da rocha apresentada na reação, que a proporção entre P/F corresponde a 6 mols de P para 2 mols de F resultando em uma relação igual a 3. Dada à diversidade de composições que os minerais que compõem as rochas apresentam, essa proporção tende a ser bastante variável (TABELA 1).

Tabela 1 - Concentração de P e F nas rochas fosfáticas

Rochas	**P**	**F**	**P/F**
	------------ g kg^{-1}	------------	
Araxá, Brasil	121	29	4,2
Patos de Minas, Brasil	104	13	8,0
Tapira, Brasil	161	15	10,7
Huila, Colômbia	91	24	3,8
Pesca, Colômbia	86	22	3,9
Sardinata, Colômbia	157	29	5,4
Bayovar, Peru	138	28	4,9
Sechura, Peru	130	28	4,6
Gafsa, Tunísia	131	36	3,6
Carolina do Norte, USA	134	35	3,8
Flórida Central, USA	143	36	4,0
Tennessee, USA	131	32	4,1

Adaptado de Chien e Mammond (1978) e Léon et al. (1986).

Numerosos processos envolvendo o reaproveitamento de subprodutos na cadeia produtiva de fertilizantes fosfatados têm sido propostos e desenvolvidos experimentalmente. Em diversos produtos e subprodutos gerados nesses processos, o F está presente em concentrações variadas. A seguir serão abordadas algumas das reações envolvendo o F na produção de ácido fosfórico, bem como os principais produtos e subprodutos contendo esse elemento, conforme descrito pela Organização de Desenvolvimento Industrial das Nações Unidas e pelo Centro Internacional de Desenvolvimento de Fertilizantes (UNIDO/IFDC, 1998).

A maioria das rochas fosfatadas contendo fluorapatita apresenta quantidade de F entre 1-4% com base em peso (CRONIN et al., 2000; LOGANATHAN et al., 2003). Em alguns casos, mais de 60% pode evoluir durante o processo de fabricação do ácido fosfórico pelo processo úmido. O remanescente de F é retido no gesso dependendo principalmente da composição da rocha e, em alguns casos, a maior parte em um filtro ácido, geralmente, 50 kg de F são volatilizados para cada tonelada de P_2O_5 (UNIDO/IFDC, 1998). Na maioria das vezes, essa volatilização ocorre na forma de SiF_4 e HF ou uma mistura dos dois gases. O F evolui nos vários estágios de produção do ácido fosfórico, sendo diferente a composição dos vapores emitidos durante os processos de reação/filtragem e no evaporador. Durante o processo de acidificação da rocha fosfática, o flúor é convertido em fluoreto de hidrogênio (HF) e, posteriormente, reage com a sílica ativa formando o fluoreto de silício (SiF_4) (reação 2).

(2) $4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$

O fluoreto de hidrogênio é parcialmente volatilizado por causa de sua pressão de vapor. O remanescente reage formando o ácido fluorsilícico que permanece no produto ácido ou como fluossilicato insolúvel que é separado como torta de filtro (reação 3).

(3) $3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$

A operação de lavagem se inicia com água pura, mas a partir de então começa a formar H_2SiF_6. A partir disso, a lavagem sempre se dará com solução de H_2SiF_6. Após o processo de reação, se o vapor de tetrafluoreto de silício for lavado com água, essa reação também ocorrerá no purificador e formará a sílica insolúvel. Para facilitar a operação, o procedimento usual consiste em purificar com uma solução diluída de ácido fluorsilícico, na qual a sílica permanece na suspensão coloidal. Em um primeiro estágio, a massa de F é separada em um sistema de purificador com ciclone e, num segundo estágio, ocorre a remoção de traços de F evitando incrustações. Vapores mais diluídos como o ar evoluído do primeiro estágio de purificação pode ser introduzido diretamente no segundo estágio de purificação.

Cerca de dois terços do F no filtro ácido é volatilizado quando o ácido fosfórico é concentrado em 50-55% de P_2O_5. Sob condição de alta temperatura e pressão reduzida obtida em evaporadores a vácuos, o ácido fluorsilícico se decompõe em tetrafluoreto de silício e fluoreto de hidrogênio que são evoluídos (reação 4).

(4) $H_2SiF_6 \rightarrow 2HF + SiF_4$

Entretanto, em concentrações de ácido fosfórico menor que 50% de P_2O_5, maior quantidade de tetrafluoreto de silício é evoluído (criação de sílica no ácido fluorsilícico circulado) devido à relação entre sua pressão de vapor e aquela do fluoreto de hidrogênio (UNIDO/IFDC, 1998). Conforme descrito, diversos subprodutos contendo F são formados durante o processamento. Nos compostos descritos, o F pode se encontrar combinado com o Si formando o ácido fluorsilícico e o fluoreto de silício. No entanto, outros elementos (e.g., Ca) podem ser adicionados em determinada etapa do processo e se combinarem com o F. Um combinado a base de Si e Ca, possível de ser obtido durante esse processamento, apresenta grande potencial de uso agrícola. Os benefícios diretos que despertam o interesse para utilização em solo seriam quanto ao fornecimento de Ca e Si, apresentando esse último elemento na forma solúvel. Contudo, existem também os efeitos indiretos que podem ser obtidos pela presença do Si e do F quanto ao poder alcalinizante associado à redução da atividade do Al^{3+} e do poder de fixação de fosfatos pelo solo.

Quanto à presença de F nesse composto, ele deverá ser avaliado em função de sua concentração no subproduto e de suas doses para uso agrícola, bem como de seus efeitos no solo e na planta. Vale ressaltar que diversos produtos e subprodutos que vêm sendo utilizados na agricultura contêm F em sua composição. Alguns processamentos para concentração de P feitos na rocha fosfática (e.g., flotação) podem aumentar ainda mais o conteúdo não somente de F, mas também de outros elementos. De acordo com estudos realizados por Conceição e Bonotto (2006), durante o processo de flotação-separação podem ser incorporados complexos solúveis contendo F e outros elementos no concentrado fosfático. Esses autores verificaram que esse processo pode incorporar até 24% de F no concentrado fosfático de Tapira (TABELA 2). Isso é esperado, pois o processo de flotação é seletivo para recuperar a apatita, a qual contém F (fluorapatita). Porém, quando se avalia a relação F/P_2O_5, nota-se que esta não aumenta durante os processos de concentração e produção. Ao contrário, pelos dados da Tabela 2, verifica-se que esta relação diminui; e.g., 7,9 mg F/g P_2O_5 na rocha, 3,5 no concentrado, 2,4 no superfosfato simples e 1,0 no superfosfato triplo.

Em outros estudos realizados na Austrália por McLaughlin et al. (1997), foi determinada a proporção de 1 g de F para cada 1 kg de P que foi igual a 271 na rocha fosfática da Carolina do Norte, a 274 na rocha fosfática parcialmente acidulada, a 256 na rocha de Hamrawein e a 170 no superfosfato simples.

Tabela 2 - Concentrações de P_2O_5, SiO_2 e F na rocha, nos fertilizantes e no subproduto da indústria de fosfatados do complexo Tapira, Brasil.

Amostras	**P_2O_5 (%)**	**SiO_2 (%)**	**F (mg kg^{-1})**
Rocha Fosfática	9,02	11,50	710
Rejeito	2,51	32,50	560
Concentrado fosfático	34,70	3,23	1074
Superfosfato simples	20,90	2,36	510
Superfosfato triplo	50,40	0,53	492
Monoamônio fosfato	56,80	< 0,1	330
Fosfogesso	1,91	1,27	210

Adaptado de Conceição e Bonotto (2006).

Com relação aos subprodutos, o fosfogesso pode conter quantidades variadas de F em função da matéria-prima, do processamento e da granulometria do material. Arocena et al. (1995) determinaram a distribuição de F no gesso derivado de diferentes rochas fosfáticas em função de diferentes frações granulométricas (TABELA 3). Observa-se que as maiores concentrações de F estão presentes nas frações mais finas do gesso.

Tabela 3 - Concentração de F (mg kg^{-1}) no gesso

Gesso	Massa Total	Frações		
		Grossa (> 53 µm)	Média (20-53 µm)	Fina (<20 µm)
Rocha de Idaho	3870	1170	2730	22000
Rocha de Togo	17670	11130	9630	45330
Rocha da Flórida	6200	4170	3570	33670

Adaptado de Arocena et al. (1995).

2.2 Fluorita e óxido de silício, processos e características

Uma das características das fluorapatitas é que no processo de acidulação com ácido sulfúrico e, ou, fosfórico (produção de superfosfato simples, superfosfato triplo, e H_3PO_4), há geração do subproduto ácido fluorsilícico. Este ácido tem sido uma constante preocupação da indústria de fertilizantes, pois sua comercialização está aquém dos volumes produzidos.

O fluorsilícico gerado em plantas de acidulação de fosfatos para fertilizantes é considerado uma grande fonte de silício (BLAKE; STICKNEY, 1966 apud HYO SHIN YU et al., 2000) e a reserva de flúor contido nas fluorapatitas é considerada quatro vezes maior que as reservas conhecidas de fluorita (CICHA ; SWANSON, 1999). Embora haja citações de que as reservas mundiais de fluorita (CaF_2) estejam sendo exauridas (VERNOOY; MICHEL, 2001), também há notificação de descoberta de novas reservas (PEÇANHA, 2007). Assim, rotas para o aproveitamento do ácido fluorsilícico como fonte de sílica e fluorita para indústria química, de vidros, cimentos, siderurgia e metalurgia têm sido estudadas, mas pouco ainda se sabe sobre uma alternativa de uso massivo para o H_2SiF_6, como por exemplo, sua neutralização com óxido de cálcio para obtenção de um produto com potencial de uso agrícola.

A geração e o manuseio (comercialização, neutralização, disposição) deste ácido estão comumente associados a questões ambientais, tanto pertinentes a solos quanto a águas. Nota-se, pois, que existe atualmente um grande desafio para se buscar destinação adequada para o grande volume do subproduto ácido fluorsilícico gerado nos processos de acidulação de rocha fosfática.

Várias alternativas para destinação de H_2SiF_6 têm sido estudadas e descartadas por problemas de custo ou qualidade final dos produtos (LAVANGA et al., 2000). Spreckelmeyer (1975) refere-se a um processo para a produção de uma fluorita sintética (CaF_2) com baixa contaminação em dióxido de silício a partir de ácido fluorsilícico (H_2SiF_6), por precipitação em uma suspensão aquosa de carbonato de cálcio. Nesta patente, o inventor cita a reação direta de ácido com a cal ou calcário, porém comenta que a precipitação conjunta de sílica e fluorita tem sido um problema, sem processo estabelecido de separação.

O problema descrito pelo inventor, quanto à precipitação conjunta de sílica e fluorita, visto sob outra ótica, pode ser uma rota de destinação de H_2SiF_6. O produto desta reação observado em microscópio caracteriza-se por cristais de fluorita incrustados de sílica. Certamente não há processo estabelecido de separação, entretanto sob o olhar de fertilização de solo, abre-se um campo ainda inexplorado, o do uso potencial deste material como um “condicionante eficientizador” do fósforo no solo, entre outras características.

A geração de H_2SiF_6 provém dos processos de acidulação de apatitas para fabricação de ácido fosfórico, e superfosfatos simples e triplo (predominantemente fluorapatitas oriundas dos fosfatos ígneos brasileiros). A via úmida é responsável pela maior parte da produção industrial de ácido fosfórico. Nesse processo, rochas sedimentares ou magmáticas contendo fosfatos de cálcio, como as portadoras do mineral fluorapatita $Ca_{10}(PO_4)_6F_2$, reagem com ácido sulfúrico conforme reação (1) já descrita.

Essa reação gera como subprodutos $CaSO_4.nH_2O$ (gesso, anidrita ou gipsita), que é removido na etapa de filtração, e o H_2SiF_6 (ácido fluorsilícico), sintetizado a partir dos gases SiF_4 e HF gerados nas etapas de acidulação, concentração e purificação do ácido.

De forma similar, na produção de superfosfatos, a fluorapatita é atacada por H_2SO_4 em concentração que varia de 58 a 65%, gerando o superfosfato simples de acordo com a reação (5):

(5) $Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF$
(6) $Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10Ca(H_2PO_4)_2.H_2O + 2HF$
(7) $Ca_{10}(PO_4)_6F_2 + 4H_3PO_4 + 20H_2O \rightarrow 10CaHPO_4.2H_2O + 2HF$

O superfosfato triplo é produzido pelo ataque da fluorapatita por ácido fosfórico conforme a reação (6) citada acima. Entre outras reações secundárias, todos os processos têm geração de HF que, em maior ou menor grau, reage com a sílica presente no processo gerando SiF_4 (HOCKING, 2005). O SiF_4 e parte do HF não reagido, por serem muito voláteis, desprendem-se na forma gasosa e são recuperados em sistema de lavagem com água.

Devido à presença de grande concentração de sílica e silicatos nos fosfatos processados no Brasil, temos pouco HF presente no ácido fluorsilícico. Durante o processamento industrial, há concentração de H_2SiF_6 nos sistemas de lavagem de gases, sendo a concentração mássica de 21 a 24% de H_2SiF_6, um limite operacional onde, a partir deste, começa aumentar o desprendimento de HF e SiF_4, o que pode comprometer a eficiência do sistema e propiciar emissões gasosas para a atmosfera (UNIDO/IFDC, 1998).

Alguns processos de acidulação permitem que o H_2SiF_6 gerado na planta seja reutilizado na própria acidulação da fluorapatita, formando fosfatos de cálcio (mono e di) e precipitando fluorita. Entretanto, poucos são os fosfatos utilizados no Brasil que permitem tal processo com eficiência, o que não ocorre usualmente com fosfatos importados de origem sedimentar. Diante disso, uma proposta alternativa é o processamento do ácido fluorsilícico para precipitação de fluorita (CaF_2) e sílica (SiO_2) para uso agrícola.

Embora a solubilidade em água do CaF_2 seja baixa (16 mg L^{-1}), a dissolução no solo depende de outros fatores tais como a concentração total de eletrólitos, íons comuns, pH e formação de complexos com ácidos orgânicos (Pickering, 1985). Da mesma forma, a presença de sílica na água é devido à dissolução da sílica baseada na seguinte reação (8):

(8) $SiO_2 + 2H_2O \rightarrow Si(OH)_4$.

A solubilidade da sílica é fortemente afetada pela temperatura, pH e presença de sais. A 25°C e pH neutro, a solubilidade da sílica está em torno de 96 mg L^{-1} (Oliveira, 2007).

2.3 Cálcio, Silício e Flúor no Solo

2.3.1 Cálcio no solo

O Ca é o principal cátion básico presente no solo. Faz parte da estrutura de diversos minerais, tais como calcita, apatita, dolomita e feldspato. Segundo Blankenau (2007), o Ca é um nutriente importante para as plantas, sendo que apenas pequena parte do total encontra-se disponível na solução do solo. Pode ser encontrado na solução do solo na forma de Ca^{2+}. Sua remoção pelas culturas e sua lixiviação, juntamente com outros cátions básicos, se tornam um dos fatores de acidificação do solo.

A deficiência de Ca^{2+} geralmente é encontrada em solos ácidos, com teores menores que 5 mg L^{-1}. Essa deficiência pode estar associada à toxidez de Al. A deficiência de Ca e toxidez de Al em camadas subsuperficiais restringem o desenvolvimento de raízes, nesses casos, as raízes da maioria das espécies cultivadas crescem apenas na camada superficial (SOUSA et al., 2007). O Ca^{2+} influi, indiretamente, no rendimento das culturas, melhorando as condições de crescimento das raízes, bem como estimulando a atividade microbiana e auxiliando na disponibilidade de Mo e na absorção de outros nutrientes, além de ajudar a reduzir o NO_3^- na planta (DECHEN; NACHTIGALL, 2007). Dessa forma, torna-se necessário realizar o suprimento contínuo desse elemento no solo para garantir o desenvolvimento adequado das culturas.

Blankenau (2007) enfatiza que o calcário e o gesso são essenciais para estabelecer o pH ótimo do solo e fornecer Ca para o crescimento do sistema radicular das culturas. Porém, há condições nas quais são necessárias quantidades maiores de Ca além das fornecidas pelo calcário. Nesse sentido, o subproduto avaliado nessa proposta poderá fornecer Ca^{2+} de forma mais efetiva devido a sua maior solubilidade, bem como, fornecer Si e reduzir a toxidez de Al^{3+}.

Em um estudo sobre a dinâmica de cátions e ânions na solução do solo, em função da aplicação de $CaCO_3$ e CaF_2 em experimento conduzido em vasos, Amaral et al. (1998), verificaram que o $CaCO_3$ foi mais eficiente em aumentar o pH. Por outro lado, nos vasos que receberam CaF_2, houve maior percolação de Al, sendo o teor de Al percolado diretamente proporcional às doses de CaF_2 aplicadas. O mesmo comportamento foi verificado para o F, que teve sua concentração na solução percolada aumentada em função das doses de CaF_2 utilizadas. Além disso, 99,5% do Al obtido na solução percolada dos tratamentos que receberam CaF_2, estava complexado com fluoreto, enquanto na testemunha, 85% do Al se encontrou na forma de Al^{3+}. Isso comprova o poder do F^- em minimizar a toxidez por Al^{3+}.

2.3.2 Silício no solo

O Si é o segundo elemento mais abundante na crosta terrestre depois do oxigênio. Ele está presente no solo, de modo geral, como um componente dos minerais da fração argila, tais como o quartzo, caulinita, micas e outros minerais silicatados. O teor de Si na fração argila diminui com o aumento do grau de intemperismo. Enquanto o quartzo, minerais silicatados, argilas silicatadas e sílica amorfa dominam a fase sólida dos solos, as formas solúveis de Si são constituídas principalmente por ácido monosilícico (H_4SiO_4), ácidos polisilícico, e complexos orgânicos e inorgânicos de Si (LINDSAY, 1979). O teor total de Si dos solos praticamente não tem relação com o Si solúvel que é o componente mais importante em relação ao crescimento das plantas. A concentração de Si solúvel no solo é dinâmica, o ácido monosilícico permanece em solução no estado monomérico em soluções neutras e levemente ácidas, porém, uma rápida polimerização acontece em altas concentrações e soluções ácidas principalmente na presença de óxidos e hidróxidos de alumínio e ferro. Por isso apesar de ser um ácido, o Si possui comportamento de base, sendo encontrado na forma não dissociada, conforme as reações (9) e (10) descritas (LINDSAY, 1979).

(9) $SiO_{2\,(solo)} + 2H_2O \leftrightarrow H_4SiO_4^0$ (log $k^0 = -3{,}10$)

(10) $H_4SiO_4 \leftrightarrow H^+ + H_3SiO_4^-$ (log $k^0 = -9{,}71$)

Várias interferências entre Si e outros íons tais como P, Al, Ca e Fe devem ocorrer em solos e modificar o comportamento do Si. Por exemplo, em solos ácidos, íons silicato e fosfato formam precipitados insolúveis que devem fixar vários outros cátions (e. g. óxidos de Fe e Al que tem uma capacidade marcante em fixar Si dissolvido na forma de H_4SiO_4). Quantidade considerável de matéria orgânica em solos inundados induz a mobilidade de Si, aparentemente devido à redução dos oxihidróxidos de Fe, que disponibilizam ácido monossilícico adsorvido (KABATA-PENDIAS, 2011).

2.3.3 Flúor no solo

A concentração de F no solo varia amplamente dependendo do material de origem, dos processos de formação e textura dos solos. Além disso, o teor de F presente nos fertilizantes aplicados no solo pode contribuir para o incremento desse elemento. Os teores mundiais de F em solos são de aproximadamente 321 mg kg^{-1}, sendo que a faixa de concentração para a maioria dos solos varia de 150 a 400 mg kg^{-1}. Existe grande correlação positiva entre o teor de F e a fração argila (KABATA-PENDIAS, 2011).

Quando o F é adicionado ao solo, grande proporção é adsorvida pelos constituintes do solo. O comportamento de F é controlado por vários parâmetros do solo, principalmente pelos teores de argila, pH e pelas concentrações de Al e P. O solo pode acumular altas quantidades de F, particularmente no horizonte B, que usualmente é enriquecido com óxidos e hidróxidos amorfos de Al (KABATA-PENDIAS, 2011). Dessa forma, a adsorção de F é maior à medida que se aumenta o teor de argila e de óxidos de Fe e Al no solo. As propriedades do solo que influenciam a partição do F entre a fase sólida e a solução encontram-se na Tabela 4.

O pH é outro fator importante que controla a sorção de F no solo. A maior sorção ocorre com valor de pH entre 5,5 – 6,5 e reduz drasticamente em maiores e menores valores de pH. A redução da sorção em menores valores de pH ocorre devido à formação de complexos com Al na solução do solo, diminuindo a concentração de F^- para sorção (MANOHARAN et al., 2007). Em maiores valores de pH, tem-se um aumento nas cargas negativas do solo, o que diminui a retenção de F^-. Nesse caso, o incremento da concentração de F^- na solução pode ocorrer devido ao seu deslocamento pelo aumento da concentração das hidroxilas no meio. Essa afinidade de flúor aos componentes da fração argila (e.g., óxidos de Fe e Al) e cátions livres na solução (e.g., Al^{3+}, Ca^{2+} e Mg^{2+}) faz com que sua mobilidade em solos seja bem menor comparada ao Cl^- e Br^-. Segundo Loganathan et al. (2001), a mobilidade de F foi similar à do P em solos que receberam fertilizantes fosfatados por longo tempo.

Tabela 4 - Propriedades do solo que influenciam a dinâmica do F em solos.

Propriedade do solo	**F**
Ph	Diminuição do pH abaixo de 5,5 e aumento acima de 6,5, aumenta a concentração de F em solução
Óxidos de Fe e Al	Diminui o F presente em solução devido à sorção
Óxidos de Mn	Não tem influência significativa
Camadas silicatadas	Diminui o F presente em solução devido à sorção
Matéria organic	Efeito indireto
Outros íons em solução	Aumenta o F em solução devido ao aumento da concentração de Al. Alta taxa de aplicação de Ca reduz a concentração de F em solução
Potencial redox (Eh)	Aumento do potencial redox tende a reduzir a sorção de F^-.

Fonte: Adaptado de Hedley et al. (2007).

O F é ligeiramente móvel em solos sob condições naturais. No entanto, em solos ácidos, a sua solubilidade aumenta devido à ocorrência de fluoretos prontamente disponíveis como NaF, KF e NH_4F. Apesar disso, outras formas como AlF_3, CaF_2 e MgF_2 são conhecidas por apresentarem uma baixa solubilidade. As formas mais comuns de F em solos são fluorapatita, fluoretos de Al e Ca, além de aluminosilicatos como $Al_2(SiF_6)_2$. Em solos calcários, a ocorrência de fluoretos levemente solúveis e complexados com Fe, Al e Si são responsáveis por uma baixa migração desse elemento. Por outro lado, em solos sódicos, o alto nível de Na trocável afeta a solubilidade de F. A sorção de F por solos ácidos é atribuída pelas interações com óxidos e hidróxidos de Al (KABATA-PENDIAS, 2011).

A mobilidade de F nos solos é variável e altamente controlada pelo pH, sua alta solubilidade ocorre em pH abaixo de 5 e maior que 6. Na solução do solo, o F ocorre tanto como complexos catiônicos (e.g., AlF^{2+} e AlF_2^+) como aniônicos (e.g., F^- e AlF_4^-). Outros pares iônicos também podem ocorrer, tais como: AlF_6^{3+}, SiF_6^{2-} e BF_4^-. Devido a sua alta afinidade pelo Al^{3+}presente na solução do solo, o F^- controla sua atividade através da formação dos complexos com esse cátion (KABATA-PENDIAS, 2011). Manoharan et al. (2007), trabalhando com solos que receberam adubações fosfatadas constataram que mais de 90% do F adicionado encontra-se na forma complexada com alumínio (AlF_3), sendo capaz de amenizar o efeito tóxico desse elemento. Esses resultados corroboram com os de Romar et al. (2009), que constataram aumentos na formação de complexos AlF_3 e AlF_4^- após a adição de fluorita em solos ácidos. Segundo esses autores, esses complexos formados apresentam menor toxidez comparado ao Al^{3+} e $AlOH^-$.

Em outro estudo, Loganathan et al. (2006) avaliaram a concentração total de F, suas formas, espécies solúveis e suas relações com as propriedades dos solos agrícolas na Nova Zelândia. Segundo os autores, a concentração total de F variou de 212 – 617 mg kg^{-1}, tendo o F total se correlacionado positivamente com o teor de P e Cd, refletindo sua ligação com o uso de fertilizantes fosfatados. O teor de F também se correlacionou positivamente com o teor de matéria orgânica e óxido de Al amorfo. A concentração solúvel de F extraída com água e com KCl 0,01 mol L^{-1} foi, respectivamente, de duas a três ordens de magnitude menores que o teor de F total. Os autores também constataram que a fração de todas as espécies de F na solução do solo foi menor que as concentrações consideradas fitotóxicas.

3 CONSIDERAÇÕES FINAIS

O Brasil é um país fortemente agrário e que possui em sua grande maioria solos muito intemperizados que necessitam da aplicação de fertilizantes e corretivos para produzir adequadamente. Grandes quantidades de fertilizantes fosfatados são produzidas e aplicadas em solos do Brasil. No entanto, no processo de fabricação destes fertilizantes o ácido hexafluorsilícico é gerado como um subproduto. Este ácido tem sido um problema para as indústrias de fertilizantes fosfatados, que estão à procura de uma adequada destinação e uso de tal rejeito.

Neste trabalho propõe-se a neutralização do H_2SiF_6 com óxido de cálcio a fim de se obter a fluorita com óxido de silício (AgroSiCa) e avaliar seus efeitos sobre as propriedades do solo e sobre o crescimento das culturas de soja e milho.

Os resultados que serão apresentados neste estudo mostrarão que a aplicação do AgroSiCa foi capaz de melhorar as condições agrícolas de solos tropicais, aumentando ligeiramente o pH dos solos e propiciando também aumentos significativos nos teores de Ca, P e Si na solução dos solos em estudo, resultando no maior crescimento e acúmulo destes elementos na parte aérea das culturas da soja e milho. O AgroSiCa ainda foi capaz de aumentar os níveis de fósforo lábil no solo, bem como de reduzir os níveis de alumínio lábil na solução dos solos.

Considerando o potencial mostrado pelos resultados experimentais, a neutralização do ácido hexafluorosilícico com óxido de cálcio pode servir como uma tecnologia sustentável para a remoção de flúor das plantas industriais, fornecendo um produto de uso benéfico na agricultura tropical que pode contribuir para aumento da eficiência da adubação fosfatada e uso mais racional das fontes de fósforo.

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SEGUNDA PARTE

ARTIGO 1

BENEFICIAL USE OF A BY-PRODUCT FROM THE PHOSPHATE FERTILIZER INDUSTRY IN TROPICAL SOILS: EFFECTS ON SOIL PROPERTIES AND MAIZE AND SOYBEAN GROWTH

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Beneficial use of a by-product from the phosphate fertilizer industry in tropical soils: effects on soil properties and maize and soybean growth

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ABSTRACT

Phosphate fertilizers are critical for crop production in tropical soils, which are known for having high phosphate-fixing capacity and aluminium saturation, as well as low pH and calcium contents. Fluorine is a component of many phosphate rocks used to make phosphate fertilizers, via a process that generates hexafluorosilicic acid (H_2SiF_6). While many treatment technologies have been proposed for removal of fluorine in industrial facilities, little attention has been given to a process of neutralizing H_2SiF_6 with calcium oxide aiming to find out an alternative and sustainable use of a by-product with a great potential for beneficial use in tropical agriculture. This study evaluated the effect of a by-product of phosphoric acid production (fluorite with silicon oxide, hereafter called

AgroSiCa) on soil properties as well as on growth of soybean and corn. Two experiments (2 crops) were conducted under greenhouse conditions in a completely randomized 3×5×2×3 factorial design as follows: three soils (Red Latosol, Red-Yellow Latosol, and Cambisol), five doses of AgroSiCa (0; 0.5; 1.0; 2.0; 4.0 t ha^{-1}), two doses of phosphorus (2×%clay and 4×%clay), with three replicates, totaling 90 plots for each experiment. The application of AgroSiCa resulted in a slight increase of soil pH. Significant increases in calcium, phosphate, and silicon levels in soil solution and in shoots of maize and soybean were observed at all doses of AgroSiCa. We also found very low levels of fluoride in all soil leachates. Significant reduction of labile aluminium was found in all soils after the cultivation of maize and soybean. In sum, AgroSiCa improved soil properties and contributed to a better growth of both crops. Our results show that reacting H_2SiF_6 derived from the wet-process phosphoric acid production with calcium oxide leads to a by-product with potential for agricultural use, especially when applied in highly-weathered soils. Besides providing calcium and silicon to plants, the use of such by-product in soils with high phosphate-fixing capacity and high aluminium saturation delivers additional benefits, since fluoride and silicon can play an important role in improving soil conditions due to the formation of less plant-toxic forms of aluminium, as well as upon decreasing phosphate fixation, thus improving root development and making fertilizer-derived phosphate more available for plant growth.

Keywords

phosphate fertilizer industry

hexafluorosilicic acid

fluoride leaching

soil solution
AgroSiCa

1 INTRODUCTION

Phosphate (P) fertilizers are critical inputs for crop production in tropical agroecosystems (Novais and Smyth, 1999). Most phosphate rocks used as raw materials for production of P fertilizers contain around 3-4% fluorine (F) (Cronin et al., 2000). When phosphate rocks are processed with sulfuric acid or phosphoric acid (for the production of single superphosphate, triple superphosphate, and phosphoric acid (H_3PO_4), hexafluorosilicic acid (H_2SiF_6) is generated as a by-product. Currently, various treatment technologies, based on precipitation, ion exchange, electrolysis, reverse osmosis membrane, and adsorption process have been proposed and tested for removal of fluorine from industrial plants (Islam and Patel, 2007), with precipitation being the most common treatment (Saha, 1993). However, they are not able to recover fluorine as a valuable industrial product. For this reason, the phosphate fertilizer industry is looking for a new, innovative, and sustainable use for this by-product. The neutralization of hexafluorosilicic acid with calcium oxide (quick lime) leads to the precipitation of fluorite and silicon oxide, resulting in a by-product (hereafter called AgroSiCa) with great potential for beneficial use in agriculture. An alternative neutralization process would be via the use of lime or calcium hydroxide. However, such processes result in a product that is very difficult to handle due to high humidity. The production and subsequent use of AgroSiCa for agricultural purposes is still a poorly explored field, especially in tropical environments with high aluminum (Al) saturation, in which fluoride can play an important role in improving soil conditions due to the formation of less toxic forms of Al, as a result of the complexation of F with Al (Whitten and Ritchie, 1991; Xei et al., 1999). Besides this, such a by-product can improve calcium (Ca) and silicon (Si) levels and decrease P fixation in highly weathered soils. All these features are relevant and justify a process of neutralizing hexafluorosilicic acid from the phosphate fertilizer industry with calcium oxide to produce a beneficial by-product for tropical agriculture use.

Many Brazilian agricultural soils are highly weathered, acidic, and of low natural fertility. They have low pH and calcium contents and are commonly saturated with exchangeable aluminum, which is toxic for most plant species. These characteristics reduce considerably the productive potential of the land, unless it is managed appropriately (Food and Agriculture Organization-FAO, 2004). Phosphorus is generally one of the most limiting nutrients in tropical agroecosystems, not only because of the natural content of such element in native soils (Novais and Smyth, 1999), but also due to the high P-fixing capacity of oxidic soils (Fink et al., 2014).

Fluoride application has been shown to be able to ameliorate Al phytotoxicity to plants (MacLean et al., 1992). However, there have been very few reports of Al-F complexing in unpolluted soils (David and Driscoll, 1984) and the effects of fluoride on crop growth in tropical soils is not usually studied. Besides its effect on decreasing Al toxicity, fluoride (Zhang and Yu, 1997) as well as silicate (Smyth and Sanchez, 1980; Pozza et al., 2007) can also decrease P fixation in variable-charge soils, due to competitive anion adsorption, which renders fertilizer-derived P more available to plants in tropical agroecosystems, thus increasing phosphate fertilizer use efficiency. Although fluoride has no direct benefits to plants, silicon is considered beneficial for most higher plants (Broadley et al., 2012).

This study evaluated the potential agricultural use of fluorite with silicon oxide, assessing its effect on soil properties as well as on growth of soybean and corn in tropical soils. We have chosen these crops because both are widely cultivated in Brazil, especially near phosphate fertilizer industries, and are the largest consumers of fertilizers in the country. Another crop with great potential for using the by-product would be sugarcane, the third biggest consumer of fertilizers in Brazil and also a crop that responds to addition of Si in tropical soils. Owing to its capability to supply Ca and Si to plants, while providing means for reducing P fixation and Al saturation, we expect to promote an innovative and sustainable use of a by-product from the wet-process phosphoric acid production in agricultural soils.

2 MATERIAL AND METHODS

2.1 By-product characterization

The chemical composition of the by-product of phosphoric acid production (AgroSiCa) was assessed following standard procedures, as recommended by Murphy and Riley (1962) for phosphorus analysis, Cheng and Bray (1951) for calcium content, Elliot and Snyder (1991) for silicon determination, and Eyde (1983) for fluoride levels. Its production process was developed by Vale S.A. (Rodrigues et al., 2014). Briefly, for P and Ca analyses, dried samples (500 mg) were weighed and acid-digested with 4.0 mL of concentrated nitric acid (HNO_3) + 2.0 mL of concentrated perchloric acid ($HClO_4$) at 120°C for 1 h and then at 220°C until $HClO_4$ fumes were observed. The total Ca content in the samples was determined using a flame atomic absorption spectrophotometer (PerkinElmer Inc., San Jose, CA, USA), and P content in the sample was determined using a spectrophotometer (S-05, Bel Photonics, São Paulo, SP, Brazil) to measure a phospho-molybdenum complex colorimetrically at 680 nm. For silicon, dried samples (500 mg) were wetted with 2 mL of 50% hydrogen peroxide (H_2O_2) in 100-mL polyethylene tubes previously rinsed with 0.1 mol L^{-1} sodium hydroxide (NaOH) and demineralized water. To each tube, 4.5 g of 50% NaOH were added at ambient temperature and gently vortexed. The tubes were individually covered with loose fitting plastic caps. The rack of tubes was placed in an autoclave at 138 kPa for 1 h. After atmospheric pressure was reached, the tubes were removed and the contents brought to 50 mL with demineralized water. Silicon concentration in the extracts was determined by the colorimetric molybdate-blue method. For fluoride, dried samples (1 g) were weighed in a beaker and reacted with 50 mL of 1.0 mol L^{-1} perchloric acid, followed by a 15-min extraction. Extracts were then filtered through filter paper into a glass to which we added 10 mL of a citrate buffer solution. A 10 mol L^{-1} NaOH solution was added to each replication until pH reached 5.7. Samples were diluted to 100 mL with distilled water and solutions were left to rest for at least 2 h before measurements. Finally, a 5-mL aliquot of each sample was mixed with 5 mL of TISAB II into a small crucible and stirred while measuring with an ion selective electrode (Model No. HI 4110, Hanna Instruments, USA). All reagents were purchased from Sigma-Aldrich, Saint Louis, USA.

The crystalline structure of AgroSiCa was analyzed by X-ray diffraction using a synchrotron light source, as described by (Costa et al. 2014), with modifications. For scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDS) analyses, AgroSiCa samples were prepared by mounting several hundred grains of each sample on aluminum stubs using carbon double sided tape and coating them with a thin film of carbon using a carbon evaporator. The samples were analyzed using a SEM (LEO EVO 40 XVP - Zeiss) equipped with backscattered (BSE) and secondary (SE) electron detectors coupled with an EDS (Quantax XFlash 5010 - Bruker). SEM-EDS monitoring analysis was conducted at a 20 kV accelerating voltage and 8.0 mm working distance and the EDS calibration was performed by using reference standard materials. After the sample was inserted into the microscope, mineral grains were selected by random vertical and lateral movements of the microscope stage to prevent operator bias in the selection of grains.

The chemical compositions of selected areas were determined by EDS on 2 or more areas of each sample to minimize errors.

2.2 Experimental design and maize and soybean cultivation

Two experiments were conducted under greenhouse conditions, using samples of three different soils collected in the cities of Lavras, Itumirim, and Nazareno, in state of Minas Gerais-Brazil. These soils were classified according to the Brazilian System of Soil Classification (Embrapa, 2006) as typic dystrophic Red Latosol, typic dystrophic Red Yellow Latosol, and typic dystrophic Tb Haplic Cambisol, respectively.

Table 1

Chemical and physical properties of the soil studied.

Properties	Red Latosol		Red-Yellow Latosol		Cambisol	
	(layer/cm)					
	0-20	20-40	0-20	20-40	0-20	20-40
pH H_2O	5.1	5.2	5.2	5.0	5.4	5.2
P (mg kg^{-1})	0.6	0.4	0.8	0.6	0.6	0.5
K (mg kg^{-1})	8	6	36	27	16	9.4
Ca ($mmol_c$ kg^{-1})	6.0	5.0	5.5	1.5	3.0	1.0
Mg ($mmol_c$ kg^{-1})	1.0	1.0	2.5	1.0	1.0	1.0
Al ($mmol_c$ kg^{-1})	1.0	1.0	5.0	5.0	8.0	8.0
H+Al ($mmol_c$ kg^{-1})	32	36	38	29	32	64
OC (g kg^{-1})	23	21	25	14	11	13
Sand (g kg^{-1})	190	190	710	690	530	530
Silt (g kg^{-1})	100	90	40	40	180	180
Clay (g kg^{-1})	710	720	250	270	290	290

soil pH-1:2.5 soil sample/water ratio; OC - organic carbon was determined was determined by the potassium dichromate ($K_2Cr_2O_7$) method; Available P and K, were determined by the Mehlich-1 method (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4); Exchangeable Ca, Mg and Al were measured by AAS on 1 M KCl extracts added with lanthanum oxide; H + Al - potential acidity was measured by 0.05 M NaOH titration of 0.5 M Ca acetate extracts at pH 7 (EMBRAPA, 1999).

For maize cultivation, we used lysimeters filled with 4 kg of soil samples from the 0-20 and 20-40 cm layers in order to mimic field conditions. For soybean cultivation, we used 5-kg pots filled with samples from the 0-20 cm layer of the same soils used for growing maize. Soil physical and chemical analyses are described in the following section and results are presented in table 1. The experimental apparatus for growing maize was set with 90 lysimeters made from polyvinyl chloride (PVC) tubes with 10 cm diameter and 20 cm height, assembled on the top of inverted 2-L polyethylene tereftalate (PET) bottles, with the same diameter and height of the PVC tube. A PET bottle cap with a hole in the center was used at the lower conical part of the lysimeter and a glass-wool layer (1 cm-thick) was spread at the bottom of each lysimeter to facilitate leaching and prevent clay illuviation. Then, 2 kg of each soil layer was poured into each lysimeter (totaling 4 kg of each soil) and tapped gently by raising and dropping the unit 5 cm from the surface four times for uniform packing.

Both experiments followed a completely randomized 3×5×2 factorial design comprising three soils (Red Latosol, Red-Yellow Latosol, and Cambisol), five doses of AgroSiCa (0; 0.5; 1.0; 2.0; 4.0 t ha^{-1}), two doses of phosphorus, added as a build-up fertilization (2×%clay and 4×%clay), with three replicates, totaling 90 plots for each experiment. AgroSiCa doses where chosen based on agronomical recommendations of Si (Camargo et al., 2007), whereas phosphorus doses are in the range of the recommended P fertilization of most crops in Brazil (Novais and Smyth, 1999; Fink et al., 2014).

In order to evaluate the effects of AgroSiCa on soil pH, an incubation curve using such by-product as well as a commercial powdered calcined lime (characterized by the manufacturer as having 35% CaO, 14% MgO, and 95.4% effective neutralizing value) was set preliminarily in all three soils. Based on soil chemical analysis and the low acidity-neutralization power of AgroSiCa, in order to growth plants, all soil samples were previously limed to increase base saturation to 50%, using the previously described commercial calcined lime. After 25 days of incubation with a moisture content near 60% of the total pore volume, the different doses of AgroSiCa were applied in the soil, and samples were then incubated for additional 25 days. Phosphorus was added (kg of P_2O_5 ha^{-1} = 2×%clay or 4×%clay) as a build-up fertilization using commercial single superphosphate (characterized by the manufacturer as having ~18% water soluble P_2O_5). Subsequently, a base fertilization was applied, which consisted of 80 mg N, 80 mg K, and 60 mg S per kg of soil, using the following sources: ammonium nitrate – NH_4NO_3 and potassium sulfate – K_2SO4. Fertilization with micronutrients consisted in the application of 3.6 mg of Mn, 1.5 mg of Cu, 5 mg of Zn, 0.5 mg of B, and 0.15 mg of Mo per kg of soil, as manganese chloride – $MnCl_2.4H_2O$, copper sulfate – $CuSO_4.5H_2O$, zinc sulfate – $ZnSO_4.7H_2O$, boric acid – H_3BO_3, and ammonium molybdate – $(NH_4)_6Mo_7O_{24}.4H_2O$. Maize and soybean plants received topdressing application of 150 mg N and K per kg of soil, split into four applications. All reagents for fertilization were purchased from Sigma-Aldrich, Saint Louis, USA. In both experiments, 10 commercial seeds of maize (Dow AgroSciences, 2B604Hx hybrid) and soybean (Embrapa/Epamig, cv BRSMG760SRR) were sown per plot, with one seedling left in each plot one week after emergence. During the experiment, soil moisture was rigorously controlled by daily weighing of the soil-plant-pot or soil-plant-lysimeter set, replacing the volume lost through evapotranspiration with deionized water.

After 45 and 60 days of treatment, for maize and soybean, respectively, the shoots in each treatment (three replicates) were harvested, washed thoroughly with distilled water and then oven-dried at

70°C until constant mass. After the maize harvest, leachates were collected following the addition of 1 L (~ one pore-volume) of distilled water in each lysimeter, applied in three equally divided portions during one hour. After the complete drainage, a whole sample was collected at once (one sample per lysimeter). Leachates were kept in dark glass bottles and stored at 4°C before analysis.

Soil solution was extracted from all plots, during the cultivation of maize and soybean plants, using 2.5-mm Rhizon® MOM soil moisture samplers (Rhizosphere Research Products, Wageningen, Netherlands). All samplers were previously cleaned with 5% nitric acid (HNO_3) and rinsed with deionized water. A sampler was inserted, obliquely, into each upper surface of the plots, and the soil solution was collected overnight to reduce effects of losses by evapotranspiration, in order to extract at least 10 mL.

2.3 Soil and plant analysis

Soil particle-size distribution was determined by the pipette method (Walter et al., 1978), for each depth and soil. Soil samples were analyzed for chemical properties using conventional methods. Briefly, available P and K were extracted following the Mehlich-1 method (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4) whereas Ca, Al, and Mg were extracted with the potassium chloride (1 mol L^{-1} KCl) method. Soil organic matter content was determined by the potassium dichromate ($K_2Cr_2O_7$) method (Embrapa, 1999). For plant analyses, leaves were ground and chemically evaluated regarding P, Ca, Si, and F levels as previously described in the by-product characterization section. Total calcium concentration was determined by flame atomic absorption spectrophotometry (PerkinElmer Inc., San Jose, USA), total P was determined by colorimetry using the molybdenum-blue method and ascorbic acid as reducing agent (Murphy and Riley, 1962), and Si by digestion with hydrogen peroxide and sodium hydroxide and then by colorimetry (Elliot and Snyder, 1991). Fluorine content of the plant material was determined by using an ion selective electrode to read F^- in 0.1 mol L^{-1} perchloric acid extracts (Eyde, 1983). The concentrations of

Ca, P, Si, and F in soil solutions extracted with Rhizon® samplers, as well as of F in soil leachates were determined as previously described.

2.4 Statistical analysis

Normality test was applied to verify if the data had a normal distribution. All results showed normal distribution. Then, data was submitted to analysis of variance (ANOVA) followed by regression analyses at a 0.05 significance level of probability.

3 RESULTS AND DISCUSSION

The chemical composition of AgroSiCa is presented in Table 2.

Table 2
Chemical characteristics of AgroSiCa.

Properties	AgroSiCa
pH H_2O	10.2
Moisture (%)	33
P_2O_5 total (%)	0.3
P_2O_5 H_2O	<LQ
P_2O_5 NAC + H_2O (%)	0.2
P_2O_5 Citric acid (%)	0.2
Ca (%)	22
Mg (%)	0.5
Si total (%)	9
Si H_2O (%)	3.6
ANP (%)	9.6
Fluoride HCl (%)	17.5
Fluoride NAC (%)	0.3
Fluoride H_2O (%)	0.03
Fluoride Citric acid (%)	0.3

soil pH-1:2.5 soil sample: water ratio; NAC: neutral ammonium citrate.

Moisture and Acid Neutralization Power (ANP) was determined according to Embrapa (1999); P-P_2O_5 was determined according to Murphy and Riley (1962). Ca and Mg was determined according to Cheng and Bray (1951). Si and fluoride were determined according to Elliot and Snyder (1991) and Eyde (1983), respectively.

The result of X-ray diffraction confirms the prevalence of fluorite (CaF_2) as the main crystalline component of the solid phase of AgroSiCa, with peaks of such mineral being identified at 3.153 Å (94 intensity), 1.931 Å (100 intensity), and lower intensity peaks at 1.647 Å (35 intensity), 1.366 Å (12), 1.253 Å (10), and 1.1150 Å (16) (Fig. 1).

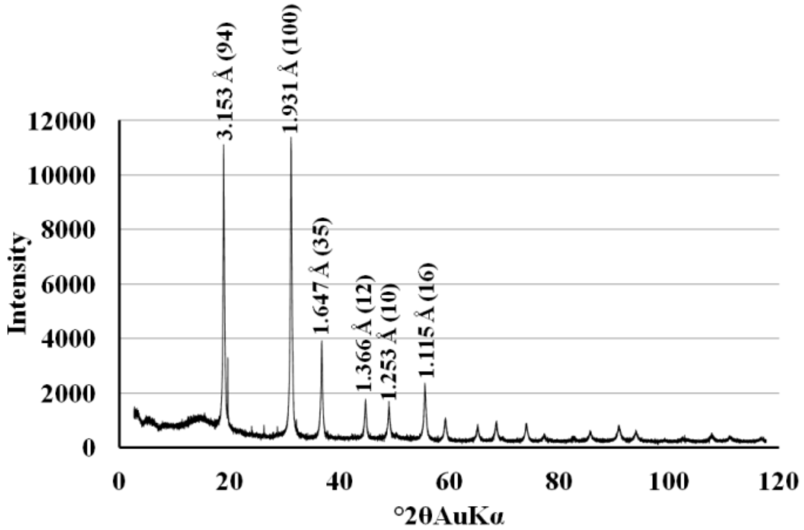

Fig. 1. X-ray diffraction patterns of AgroSiCa showing representative peaks of fluorite.

Analyses of MEV-EDS revealed the co-occurrence of Ca, F, Si, and oxygen (O), with Ca more associated with F, and Si more associated with O, in a heterogeneous mass of mixed amorphous and crystalline materials of micrometric size (Fig. 2).

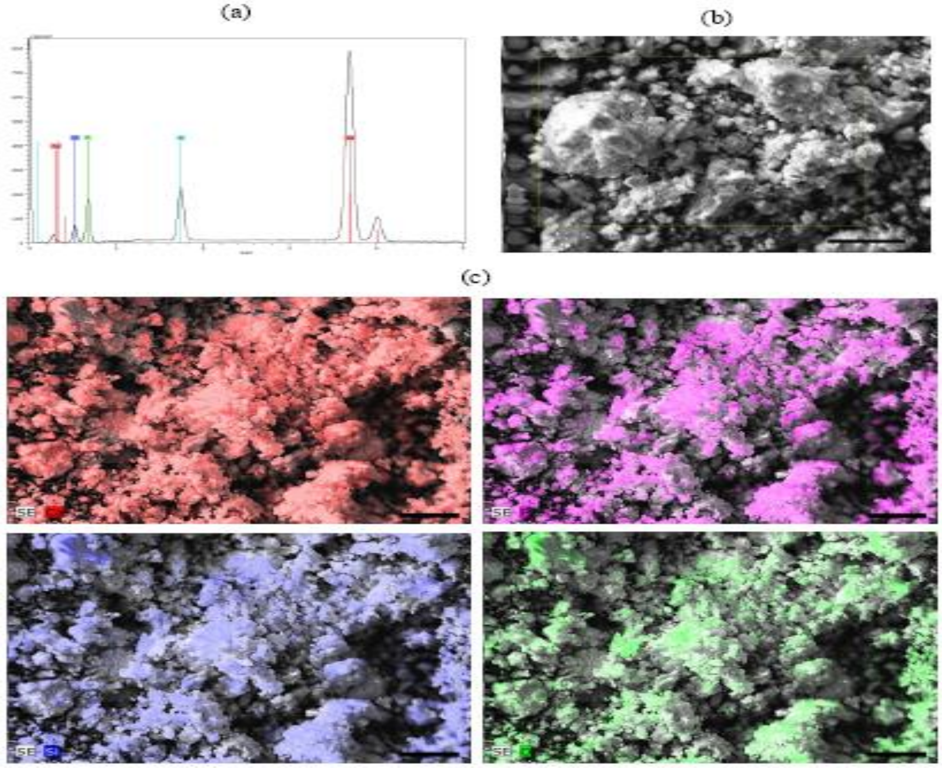

Fig. 2. SEM and EDS mapping images of AgroSiCa grains. (a) The EDS spectrum of the particle (wt%: Ca = 40.1; F = 25.7; O = 15.5; Si = 4.8). (b) A detailed image of the particles shape (Scale bar: 10 µm). (c) An elemental mapping of the most relevant elements in the particles (Scale bar: 20 µm). Ca, F, Si, and O Si are coexistent, with Ca more associated with F, and Si more associated with O.

The effects of AgroSiCa on soil pH, as compared with lime, are shown in Figure 3.

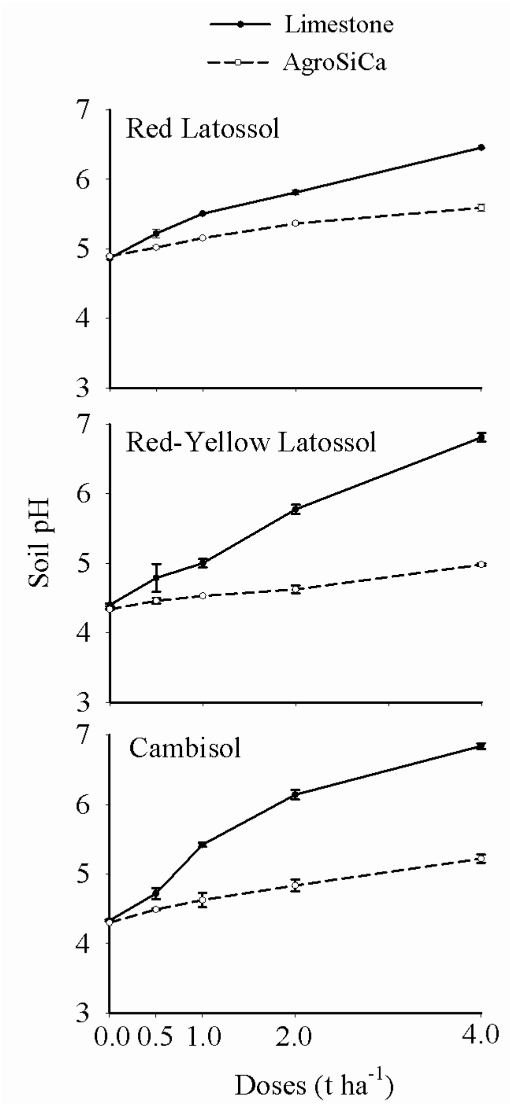

Fig. 3. Soil pH ($CaCl_2$) after 40 days of incubation of three soils with AgroSiCa and limestone.

After 40 days of incubation, the application of AgroSiCa resulted in a slight increase in soil pH, yet the effects are not comparable with the ones obtained with equivalent doses of calcined lime, due to the low acidity-neutralization power of AgroSiCa. The increase in soil pH after application of AgroSiCa is due to the fact that the product contains silicate materials (~9% Si-total, 40% being soluble in water), which dissolve promoting the release of a hydroxyl (OH^-), neutralizing hydrogen ion (H^+) and raising the soil pH, as observed elsewhere (Camargo et al., 2007). Previous studies have also indicated that the addition of fluoride can increase soil pH due to the displacement of OH^- from clay adsorption sites or Al-OH species by fluoride ion (F^-) (Wenzel and Blum, 1992). In fact, AgroSiCa may have increased soil pH because of both, its basic character as well as the release of OH- from iron (Fe) and Al oxides/hydroxides and also from the surface of clay minerals due to fluoride adsorption (McBride, 1994), a process that involves ligand exchange with a coordinated OH group (Omueti and Jones, 1977).

Following the application of increasing doses of AgroSiCa combined with two different doses of P_2O_5 (2×%clay and 4×%clay), the ANOVA did no shown significant differences for soil attributes (P, Ca, Si, and F in soils solution, and exchangeable Al in soil) or plant growth parameters (maize and soybean) between the doses of P added. Therefore, subsequent results are presented considering both doses together.

The application of increasing doses of AgroSiCa increased the contents of phosphorus, calcium, silicon, and fluoride in soil solution (Fig. 4).

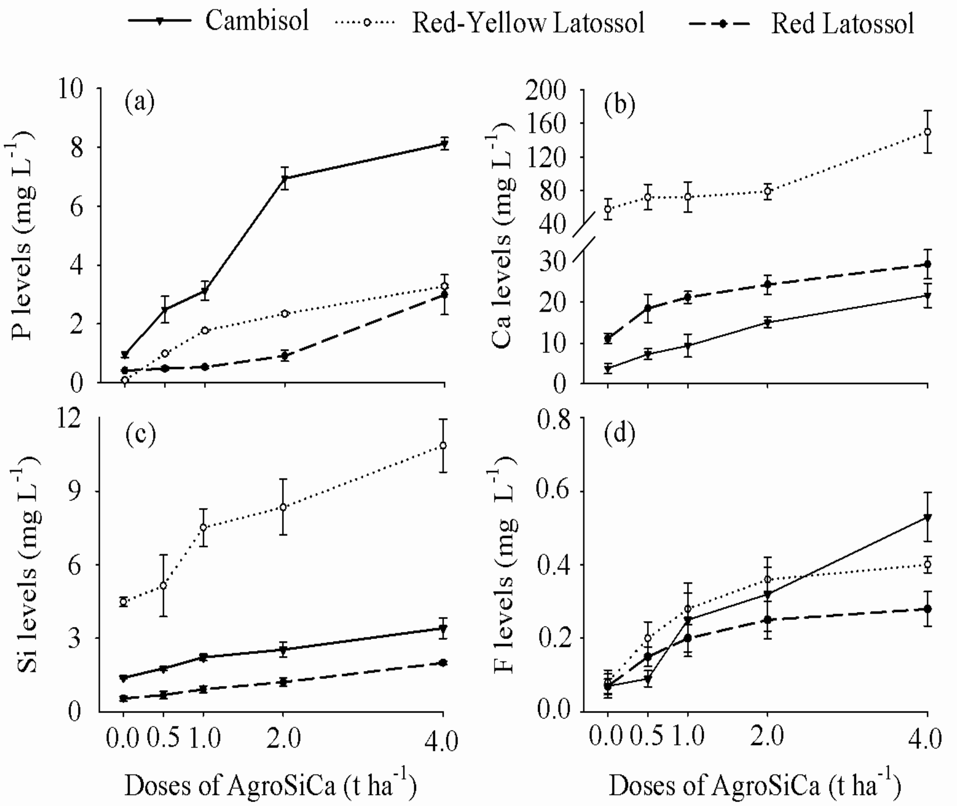

Fig. 4. Levels of P (a), Ca (b) and Si (c) in soil solution, during maize and soybean cultivation, and levels of F (d) in soil leachates after maize cultivation, as a function of doses of AgroSiCa in different soils.

Significant increases in soil solution levels of P and Ca – two important plant macronutrients – were observed at all rates applied (Fig. 4A and 4B). Such results are relevant as these nutrients often limit the growth of most crops (e.g., maize and soybean) in tropical agroecosystems (Novais and Smyth, 1999; FAO, 2004). The observed increasing levels of calcium in soil solutions following the application of AgroSiCa are related to the chemical composition of AgroSiCa, since the applied product has 22% Ca (Table 2). Increasing phosphorus concentrations in solution may be related to phosphate-silicate and phosphate-fluoride competition for sorption sites, as the product formed after the neutralization reaction of hexafluorosilicic acid with calcium oxide contains Si and F (Table 2). It is well established that phosphate and silicate ions are adsorbed by iron and aluminum oxides, with silicate being able to displace the previously adsorbed phosphate from oxidic surfaces. The chemical similarity of the two anionic forms is largely responsible for this behavior (McKeague and Cline, 1963). In fact, application of silicate previously to phosphate favors the bioavailability of P in highly weathered soils (Pozza et al., 2007). In addition to silicate, fluoride is also known to be able to replace phosphate on positive charges of oxidic soils (Zhang and Yu, 1997).

Besides increasing the soil solution content of two important macronutrients, i.e. P and Ca, the application of AgroSiCa increased also the concentration of Si in soil solution (Fig. 4C), with a greater effect in the Red-Yellow Latosol (with the highest sand content, and thus the lowest sorption capacity), when compared with the Red Latosol and the Cambisol. The increased concentration of Si in soil solution indicates that the source of Si used is soluble and very effective in delivering Si, contributing to increasing P availability in the soils, as previously mentioned. Souza et al. (2008) also found an increase in soil pH and a reduction in Al toxicity, as well as an increased in labile P levels in four acid soils, after application of calcium silicate. The increased availability of Si in soil solution may have contributed to a better growth of maize and soybeans plants, as this element is considered beneficial for higher plants (Broadley et al., 2012).

The occurrence of dissolved fluoride in soil solution is often associated with high pH (Agarwal et al., 2003; Chae et al., 2007), a situation that can hardly be found in weathered soils. Groundwater contaminated by fluoride leaching has been a concern especially in temperate regions. On the other hand, very little is known about the dynamics of fluoride and its possible beneficial effects as a soil amendment, or its effects in crops growing in tropical regions such as Brazil. In general, total fluoride in the soil is considered a poor soil pollution status indicator due to great natural variation and differences in sorption strength and sorption capacity amongst soils (Arnesen, 1997; Cronin et al., 2000; Loganathan et al., 2001). Therefore, fluoride in soil solution is probably a better indicator of the availability of such element to plants.

In the present study we found very low levels of fluoride in soil solution, irrespectively of the soil or the doses of AgroSiCa applied (Fig. 4D). If we compare our results with the maximum permissible concentration of fluoride in drinking water, we note that all measured concentrations fell below the maximum acceptable level of 1.5 mg L^{-1}, as defined by the World Health Organization (Who, 2011). These results demonstrate that the application of AgroSiCa will not lead to unsafe levels of fluoride in groundwater, and even contributes to the exchange of ligands with the formation of Al-F and Al-OH complexes, which may increase P availability to plants. Murray (1983) also found low levels of fluoride in leachates from sandy soils, reporting decreasing amounts of fluoride with time, due to binding of this element in various soil components.

We found that the application of AgroSiCa significantly reduced exchangeable Al levels in all three soils, after the cultivation of maize and soybean (Fig. 5), which certainly contributed to the higher growth of both crops.

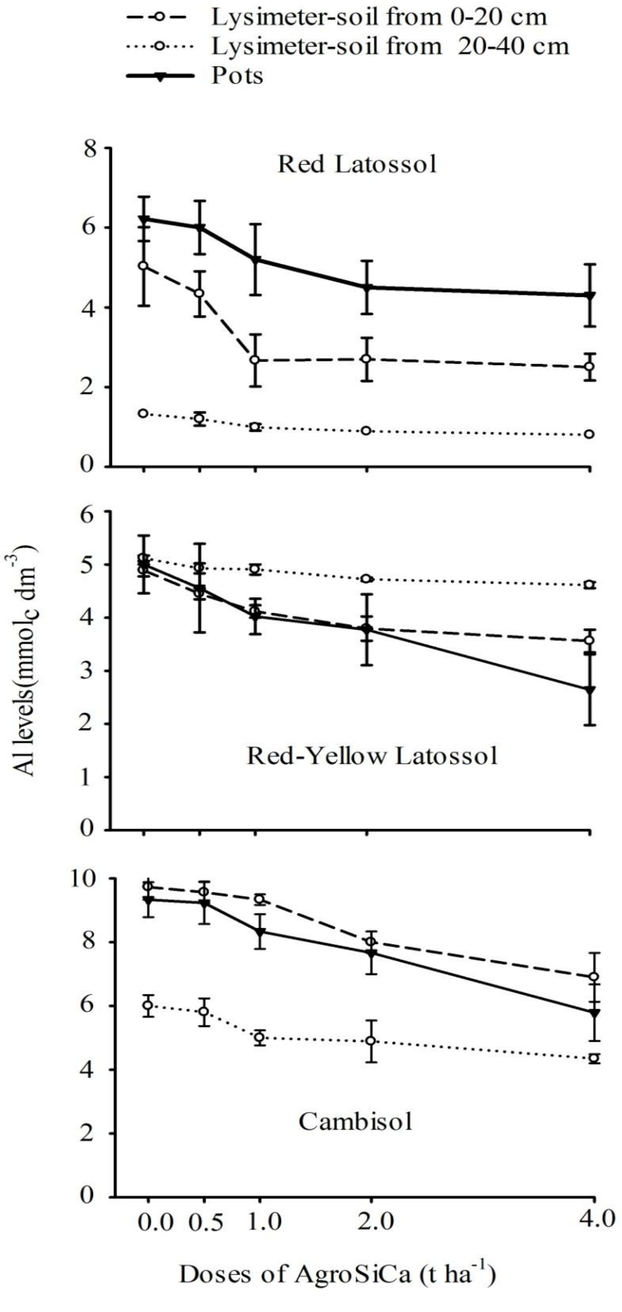
Lysimeter-soil from 0-20 cm
Lysimeter-soil from 20-40 cm
Pots
Red Latossol
Red-Yellow Latossol
Cambisol
Al levels(mmol$_c$ dm^{-3})
Doses of AgroSiCa (t ha^{-1})
0.0
0.5
1.0
2.0
4.0
0
2
4
6
8
0
1
2
3
4
5
6
0
2
4
6
8
10

Fig. 5. Exchangeable Al levels in three soils treated with increasing doses of AgroSiCa, after maize and soybean cultivation.

This result is relevant, as it supports the beneficial agricultural use of the product formed after the neutralization reaction of hexafluorosilicic acid with calcium oxide, especially when it is applied in tropical soils that are weathered and highly saturated with aluminum ion (Al^{3+}). The chemical behavior of Al and F in soil ecosystems has been paid attention to because the Al^{3+} can be complexed with the fluoride ion in soil solution of acidic soils ($pH < 6.0$) (Xie et al., 1999). Such reaction is important, because Al complexed with ligands such as F^- is considered less toxic to plants (Whitten and Ritchie, 1991).

As a consequence of the reduction of Al phytoavailability and the increased nutrient availability in the soils, as previously mentioned, we found that the application of AgroSiCa provided an increase in shoot yield for both crops (maize and soybean) (Fig. 6), with the effect being more pronounced in the Cambisol, which had the highest Al content (Table 1).

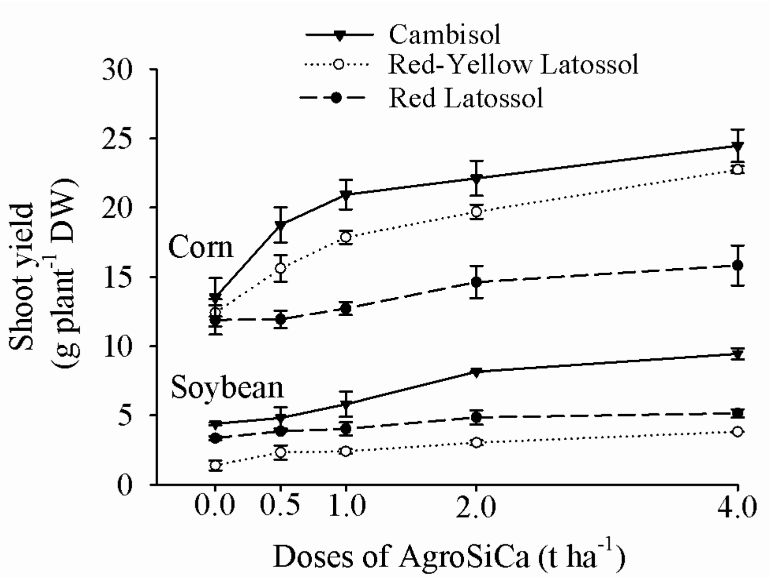

Fig. 6. Shoot yield of maize and soybean in three soils treated with increasing doses of AgroSiCa.

These results, again, show the potential for the beneficial agricultural use of the product obtained by recovering hexafluorosilicic acid from wet-process phosphoric acid production, and mixing it with calcium oxide, especially when applied in weathered soils.

The effects of the application of AgroSiCa on elemental accumulation in maize and soybean shoots are shown in table 3. The P, Ca, and Si levels in shoots were significantly increased following the application of AgroSiCa in the soil, and the response varied according to the soil. These results can be related to the chemical composition of the product applied in the soil and the interactions of fluoride and silicon with soil colloids, as previously discussed. We also found an increase in fluoride levels in both maize and soybeans shoots (Table 3). However these levels did not promote toxic effects in these crops. In fact, even though the total fluoride content of AgroSiCa was ~17%, the citrate- and neutral ammonium citrate (NAC)-extractable levels – which are much more related to phytoavailable levels of F – are very small (~0.3%). Furthermore, in the soil, fluoride is found mostly forming insoluble chemical compounds, which can explain the low toxicity in some plants (Macêdo and Morrill, 2008). We found fluorine levels in maize plants lower than those reported by Fortes et al. (2003), who described fluorine toxicity in maize plants near a ceramic industry, and lower than those found by Domingues et al. (2011), who studied the susceptibility of guinea grass and maize varieties to fluoride. Our reported values were also smaller than those observed by Haidouti et al. (1993), who studied fluorine levels on plants growing near an Al industry in Greece. Also, the fluorine levels found in our study for soybean plants were lower than those reported by Mustofa et al. (2014) for staple cereals and legumes.

Table 3

Total levels of P, Ca, Si, and F in leaves of maize and soybean treated with increasing doses of AgroSiCa.

Doses (t/ha)	Red Latosol				Red-Yellow Latossol				Cambisol			
	Ca	P	Si	F	Ca	P	Si	F	Ca	P	Si	F
		(g kg^{-1})		(mg kg^{-1})		(g kg^{-1})		(mg kg^{-1})		(g kg^{-1})		(mg kg^{-1})
	Corn											
0	2.53±0.4	1.05±0.05	2.78±0.48	49.46±2.90	3.00±0.33	1.81±0.05	2.81±0.42	49.11±3.11	1.67±0.04	1.81±0.11	2.71±0.28	30.90±2.82
0.5	2.83±0.2	1.12±0.18	2.23±0.24	50.41±4.00	3.56±0.36	1.92±0.08	2.43±0.27	53.65±3.53	1.96±0.31	1.99±0.12	2.26±0.26	46.05±3.19
1.0	2.70±0.3	1.25±0.15	2.35±0.31	47.36±2.54	3.76±0.62	2.00±0.10	2.55±0.12	57.00±3.4	2.43±0.11	2.10±0.13	2.53±0.30	59.00±2.18
2.0	3.27±0.2	1.25±0.15	1.95±0.35	49.45±3.23	3.86±0.42	2.10±0.12	2.75±0.47	64.00±3.33	3.46±0.24	2.55±0.18	3.03±0.30	72.00±3.83
4.0	3.07±0.2	1.63±0.18	2.43±0.24	47.36±0.86	4.30±0.06	2.20±0.06	3.12±0.32	80.00±8.11	3.63±0.28	2.70±0.10	3.66±0.23	98.00±7.80
	Soybean											
0	2.99±0.9	0.97±0.06	0.50±0.03	0.03±0.09	4.51±0.51	1.09±0.06	0.90±0.45	2.24±0.84	3.07±0.90	1.10±0.16	0.70±0.28	1.47±0.90
0.5	4.41±0.7	1.00±0.05	0.80±0.12	0.04±0.01	5.47±0.15	1.23±0.03	1.20±0.32	3.13±1.31	3.45±0.38	1.21±0.09	0.98±0.26	1.58±1.20
1.0	4.42±0.7	1.11±0.04	1.30±0.31	0.17±0.09	6.59±1.14	1.32±0.05	1.30±0.12	3.49±1.38	3.95±0.54	1.27±0.04	1.66±0.30	6.11±2.11
2.0	5.51±1.1	1.14±0.04	1.70±0.35	0.21±0.12	7.98±0.76	1.35±0.06	1.80±0.23	3.84±1.67	4.89±0.78	1.30±0.07	2.32±0.30	8.67±1.87
4.0	6.33±0.7	1.19±0.03	1.82±0.24	0.89±0.15	9.32±0.65	1.40±0.09	2.43±0.44	4.74±0.56	5.71±0.44	1.46±0.05	3.01±0.43	9.34±1.13

Standard error of the mean (n=5)

4 CONCLUSIONS

In conclusion, results described in this study provide an important understanding of the processes governing the agricultural use of a by-product from the wet-process phosphoric acid production. The results confirm that the application of AgroSiCa in tropical soils favors plant growth, reduces Al toxicity in soil, and increases levels of P, Ca, and Si in soil and plants. Furthermore, low levels of fluoride were observed in soil leachates, as well as in plants, following the application of agronomic doses of AgroSiCa. Considering the potential shown by our experimental results, the neutralization of hexafluorosilicic acid with calcium oxide can serve as a sustainable technology for removal of fluorine from industrial plants, while providing a product with beneficial use in tropical agriculture.

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ARTIGO 2

EFFECTS OF APPLICATION OF AGROSICA IN PHOSPHORUS AND ALUMINUM FRACTIONS IN TROPICAL SOILS

Artigo que será submetido ao periódico: Environmental Science: Process & Impacts

Effects of application of AgroSica in phosphorus and aluminum fractions in tropical soils

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ABSTRACT

The hexafluorosilicic acid (H_2SiF_6) is a by-product generated in the phosphate fertilizer industry that has caused problems to these industries due to marketing difficulties and proper disposal of large quantities of H_2SiF_6 produced. However, the H_2SiF_6 neutralization process with calcium oxide leads to precipitation of fluoride with silicon oxide (AgroSiCa) may be the adequate and sustainable destination of H_2SiF_6. In tropical countries are used large quantities of phosphate fertilizers in order to get a good crop yields, since these soils, phosphorus is often the most limiting plant nutrient. Another feature which limits agricultural production is high toxic aluminum levels found in these soils. However, phosphorus and aluminum may be found on different fractions and forms in soil and soil solution. Therefore the fractionation of P and Al in the soil allows to study the dynamics and the availability of P and phytotoxicity of aluminum more accurately, so, this manuscript aimed to study more deeply the effects of the application of AgroSiCa through of fractionation of P and Al in different layers of tropical soils. The experiment was conducted in a greenhouse conditions in completely randomized design consisting of 3 soils (Red Latosol, Red-Yellow Latosol, and a Cambisol), 3 doses of AgroSiCa (0, 2.0 and 4.0 t ha-1), 2 layers, more 1 treatment control of each soil, with 3 replications. Then, 2 kg of each soil layer was poured into each lysimeter (totaling 4 kg of each soil). After incubation time with AgroSiCa, the lysimeters were sectioned into 0-10 cm and 30-40 cm for the collection of soil and soil solutions in the respective layers for analyses of fractions of P and Al. The application of AgroSiCa provided a reduction of labile aluminum content in the soil solution and increased of labile phosphorus fraction in all soils studied, both important factors for better crop production in tropical soils.

Keywords

Phosphate fertilizer industry;

AgroSiCa;

Aluminum;

Phosphorus;

Fractionation;

1 **INTRODUCTION**

The production process of phosphate fertilizer and phosphoric acid by phosphate rock acidulation with sulfuric or phosphoric acid produces hexafluorosilicic acid (H_2SiF_6) as by-product. Although part this by-product is sold to the industry, the total production is always greater than the demand. Therefore, the phosphate fertilizers industry is presently looking for a destination for H_2SiF_6. Until recently, different alternatives for the allocation of H_2SiF_6 were unsuccessfully due to high costs and low quality of the finished product. However, the H_2SiF_6 neutralization process with calcium oxide proposed by Rodrigues et al. 2016 leads to precipitation of fluoride with silicon oxide (AgroSiCa) (Figure 1), which is a product of easy handling and agricultural application.

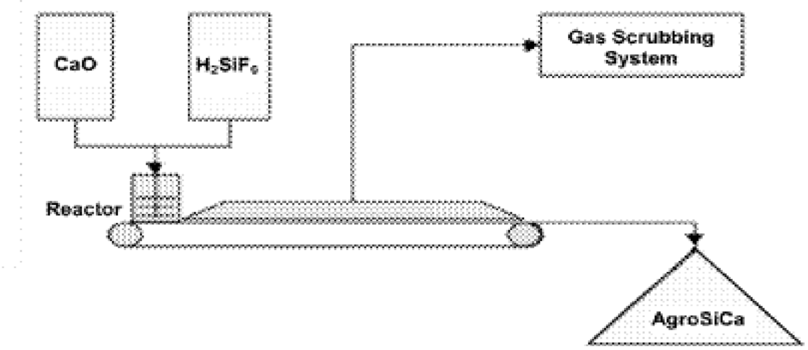

Fig 1. Production Process of AgroSiCa.

Therefore the production and agricultural use of AgroSiCa may be the adequate and sustainable destination of H_2SiF_6. The AgroSiCa contains: calcium (Ca) and phosphorus (P), two nutrients required in large amounts by crops; silicon (Si), an beneficial element for plants; and fluoride (F) (Valle et al., 2016). In our previous study, Valle et al., (2016) found promising results with the application of AgroSiCa in tropical soils. This study showed an slightly increased soil pH, decreased exchangeable aluminum levels in soils and increases levels of Ca, P and Si in the soil solution, resulting in increased growth and accumulation of these elements in shoots of soybean and maize.

It should be emphasized the added benefit of capturing fluorine to reduce their emission to atmosphere for a sustainably process. Moreover, the use of AgroSiCa will provide a better utilization of phosphate fertilizers providing greater longevity on the exploitation of a finite and non-renewable resource of P. A possibility potential to assist with sustainable solutions that involve a future of uncertainty about food shortages associated with P scarcity, before it becomes a crisis (Childers et al., 2011).

Tropical soils are acidic, highly weathered, rich in iron and aluminum oxides, and present low fertility and high P retention capacity, making this element less available to plants. However, P may be retained with different binding energies on soil colloids. Therefore, there are P fractions in the soil which are more labile and more available to the plants and others are less labile or non-labile they are retained with higher binding energies in the solid phase of the soil and are less available to plants (Heldey et al., 1982.; Novais e Smith 1999.; Lopes et al, 2012.; Fink et al, 2014). An understanding of P fractions that predominates in the soil allows us to infer more precisely the AgroSiCa's effects on P dynamics and the availability to plants. Valle et al., (2016) as mentioned previously, found significant increases in P total levels in soil solution with the application of AgroSiCa.

Another problem for crop production is the phytotoxicity caused by Al present in the soil solution in forms considered toxics, also very common in tropical agroecosystems. This element prevents proper root growth, causing less absorption of water and nutrients, with substantially impact in crop yields (Kinraide, 1991; Samac and Tesfaye, 2003). Aluminum total concentration cannot be used as parameter to assess their toxicity to plants and their environmental damage (Boudot et al., 2000; Matúš and Kubová, 2005). Some Al species as Al_3^+, hydroxyl-Al [$AlOH^{2+}$; $Al(OH)_2^+$; $AlSO_4^+$] are considered more toxic to plants (Blamey et al., 1983; Li et al., 1989; Barcelo et al., 1993), while other are considered non-toxic, such as: the precipitate form as $Al(OH)_3$ and the complexed form with fluoride, as AlF^{2+}; AlF_2^+; AlF_3^0, and AlF_4^- or with organic matter (Baylis et al., 1994; Kinraide, 1991; MacLean et al., 1992; Suthipradit et al., 1990).

Therefore, assessment of toxicity of aluminum in the soil can more appropriately performed by speciation to estimate the concentration of species in the soil solution (James et ai, 1983; Driscoll, 1984; Berggren 1989; Clarke, 1992; Whitten et al, 1992; Matúš e Kubova, 2005), combined by extraction under the recommended conditions to quantification of labile and non-labile species in solution (Boudot et al., 1994).

Our previous study showed positive results in the application of AgroSiCa in tropical soils with regard to the increase of P in soil solution and reduction of exchangeable Al levels in the soil, two of the main characteristics that contributed to increased production of maize and soybean (Valle et al., 2016). However, P and Al can be found in different fractions and species in soil and soil solution, so, this study aimed to study more deeply the effects of the application of AgroSiCa through of fractionation of P and Al in tropical soils.

2 MATERIALS AND METHODS

2.1 Experimental design

The experiment was conducted under greenhouse conditions, using lysimeters filled with 4 kg of soil material from the 0-20 and 20-40 cm layers of three different soils collected in the cities of Lavras, Itumirim, and Nazareno, in state of Minas Gerais-Brazil. These soils were classified according to the Brazilian System of Soil Classification (Embrapa, 2006) as Latossolo Vermelho distrófico típico (LVd), Latossolo Vermelho-Amarelo distrófico típico (LVAd), and Cambissolo Hálico tb distrófico típico (CX). Soil particle-size distribution was determined by the pipette method (Walter et al., 1978), for each depth and soil. Soil samples were analyzed for chemical properties using conventional methods. Briefly, available P and K were extracted following the Mehlich-1 method (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4) whereas Ca, Al, and Mg were extracted with the potassium chloride (1 mol L^{-1} KCl) method. Soil organic matter content was determined by the potassium dichromate ($K_2Cr_2O_7$) method (Embrapa, 1999).

Table 1

Chemical and physical properties of the soil studied.

Properties	Red Latosol		Red-Yellow Latosol		Cambisol	
	(layer/cm)					
	0-20	20-40	0-20	20-40	0-20	20-40
pH H_2O	5.1	5.2	5.2	5.0	5.4	5.2
P (mg kg^{-1})	0.6	0.4	0.8	0.6	0.6	0.5
K (mg kg^{-1})	8	6	36	27	16	9.4
Ca ($mmol_c$ kg^{-1})	6.0	5.0	5.5	1.5	3.0	1.0
Mg ($mmol_c$ kg^{-1})	1.0	1.0	2.5	1.0	1.0	1.0
Al ($mmol_c$ kg^{-1})	1.0	1.0	5.0	5.0	8.0	8.0
H+Al ($mmol_c$ kg^{-1})	32	36	38	29	32	64
OC (g kg^{-1})	23	21	25	14	11	13
Sand (g kg^{-1})	190	190	710	690	530	530
Silt (g kg^{-1})	100	90	40	40	180	180
Clay (g kg^{-1})	710	720	250	270	290	290

soil pH-1:2.5 soil sample/water ratio; OC - organic carbon was determined was determined by the potassium dichromate ($K_2Cr_2O_7$) method; Available P and K, were determined by the Mehlich-1 method (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4); Exchangeable Ca, Mg and Al were measured by AAS on 1 M KCl extracts added with lanthanum oxide; H + Al - potential acidity was measured by 0.05 M NaOH titration of 0.5 M Ca acetate extracts at pH 7 (EMBRAPA, 1999).

The experiment was conducted in a completely randomized factorial design 3 x 3 x 2 consisting of 3 soils (Red Latosol, Red-Yellow Latosol, and a Cambisol), 3 doses of AgroSiCa (0, 2.0 and 4.0 t ha^{-1}), 2 layers, more 1 treatment control of each soil, with 3 replications.

Then, 2 kg of each soil layer was poured into each lysimeter (totaling 4 kg of each soil) and tapped gently by raising and dropping the unit 5 cm from the surface four times for uniform packing.

The three soils were incubated with by-product as well as quick lime (35% CaO, 14% MgO, 95.4% effective neutralizing value), were previously limed to increase pH to 5.5, except the control treatment (which was not applied lime or AgroSiCa).

After 25 days of incubation with moisture content near 60% of the total pore volume, the two doses of AgroSiCa (2.0 and 4.0 t ha^{-1}) were applied in the soil, and samples were then incubated for additional 25 days. The doses were chosen based on agronomical recommendations of Si (Korndörfer et al., 2004; Camargo et al., 2007). Subsequently, phosphorus was added (kg of P_2O_5 ha^{-1} = 2× % clay) as a build-up fertilization using commercial single superphosphate (characterized by the manufacturer as containing ~18% water soluble P_2O_5).

Later, all lysimeters were sectioned into 0-10 cm and 30-40 cm and the soil of each layer was transferred to disposable plastic cups, where soil samples were collected to conduct the fractionation of P as well as soil solutions samples for the fractionation of Al. Soil solution was extracted from all soils using 2.5-mm Rhizon® MOM soil moisture samplers (Rhizosphere Research Products, Wageningen, the Netherlands). All samplers were previously cleaned with 5% HNO_3 and rinsed with deionized water. A sampler was inserted, obliquely, into each upper surface of the plots, and the soil solution was collected overnight to reduce effects of losses by evapotranspiration, in order to extract at least 10 mL.

2.2 Analytical procedures to determination of aluminum in soils solutions

2.2.1 Total aluminum determination

Total Al may be determined by inductively coupled plasma atomic emission spectroscopy (ICPAES) on pre-acidified samples (pH ≅ 2).

2.2.2 Labile aluminum determination

Labile aluminum was obtained according to Boudot et al. (1994). The method consists of the flash extraction (5 s) with a pH 5 buffered 8-hydroxyquinoline reagent of the monomeric inorganic Al species. The method excluded the Al–F species.

2.2.3 Non-labile aluminum determination

The non-labile Al contents were determined by the difference between the total and labile Al.

2.3 Analytical procedures to determination of phosphorus fractions in soils

We proceeded the subdivision of P fractions in P-Resin + $NaHCO_3$ (P res + $NaHCO_3$), P-NaOH 0,1 M and P-NaOH 0,5 M in order to better understand the dynamics and nutrient availability in soil. For the phosphorus fractionation in soils successive extractions were applied to the same sample, with adapted method of Hedley et al. (1982). This fractionation, the labile forms (more available to plants, consisting in soluble phosphates in water and chemisorbed with low energy in the soil solid phase) are extracted by $NaHCO_3$ 0.5 M and anion exchange resin. The fraction extracted by NaOH 0.1 mol L^{-1}, consisting in organic forms bound in humic acid and those chemisorbed with average power in oxides and kaolinite (Hedley et al., 1982), according to Mc Laughlin et al., 1977 and Bowman & Cole, 1978 are forms that can be considered moderately labile and forms extracted by NaOH 0.5 M represent those chemisorbed with high energy, more associated to Fe, Al oxides and humic compounds (Rheinheimer et al., 2008).

In the extraction with resin were used mesh polyethylene bags 400 μM containing 0.6 g of resin anion exchange-X18 DOWAX2 saturated with bicarbonate. The common procedures to all fractions were using a 50 mL centrifuge tubes; agitation of the suspensions in-circular horizontal shaker at 220 rpm; 5,000 rpm centrifugation for 5-8 minutes and agitator type vortex; Transfer the extract plus rinse solution for the same volumetric flask up to volume with deionized water and determination of P in the extracts by Murphy and Riley method (1962).

Some extractors are effective to quantify available soil P, such as ion exchange resin (Raij & Quaggio, 2001) and extraction by $NaHCO_3$

0,5 M, since the P extracted by these methods is available to plants (Schmidt et al., 1996; Guo & Yost, 1998; Gatiboni et al., 2007).

3 **RESULTS AND DISCUSSION**

The chemical composition of AgroSiCa, their main crystalline phases, and the effects of AgroSiCa on soil properties and growth of soybean and corn were presented in our previous study (Valle et al. 2016). Briefly, we observed significant increases in calcium, phosphate, and silicon levels in soil solution and in growth of maize and soybean at all doses of AgroSiCa. We also found very low levels of fluoride in all soil leachates. In sum, AgroSiCa improved soil properties and contributed to a better growth of both crops.

The total, labile and non-labile aluminum levels are shown in Figure 2.

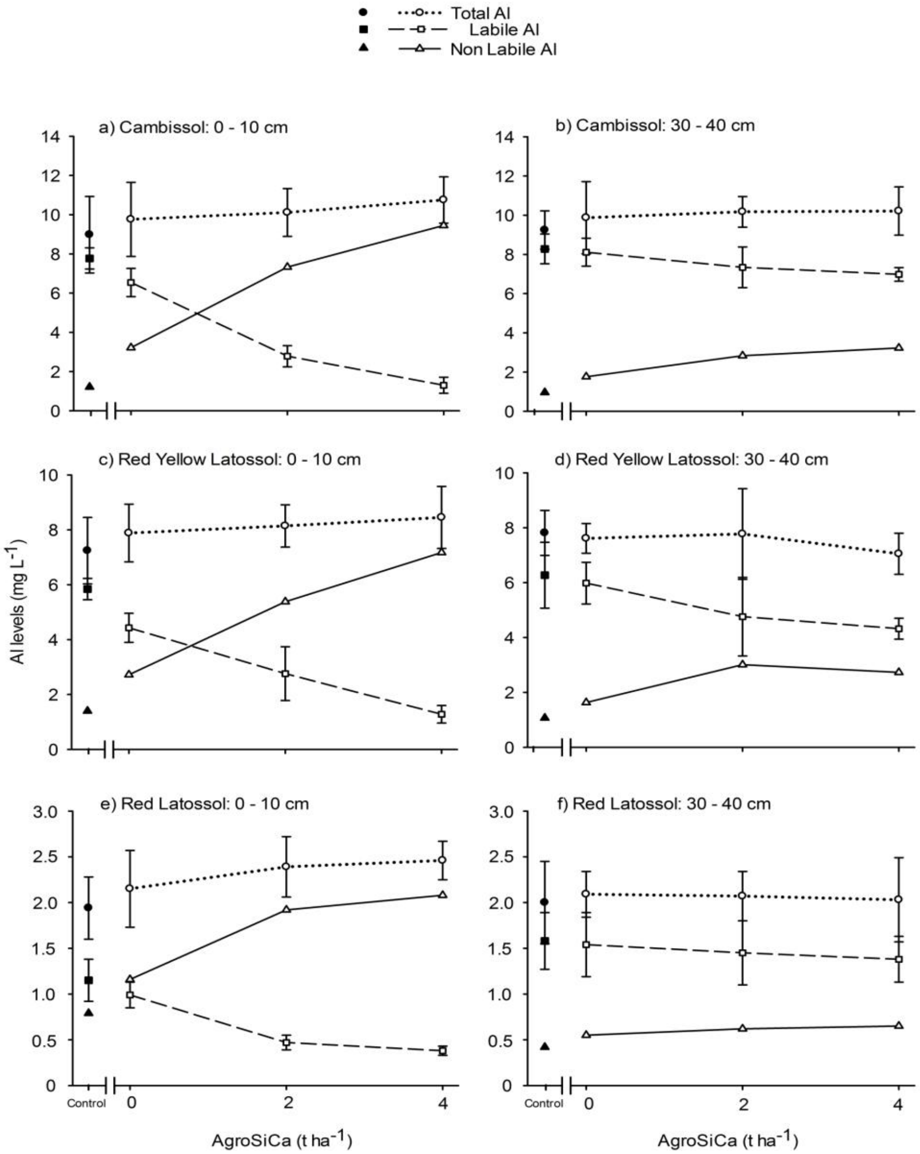

Fig 2. Total, labile and non-labile aluminum levels according to the doses of AgroSiCa.

The increasing doses of AgroSiCa did not vary the total aluminum (Al_T) content in each depth of soils. The dose 0 of AgroSiCa, in the 0-10 cm layer, showed Al_T values of 8.98, 7.24 and 1.94 mg L^{-1}, respectively, for Cambissol, Red Yellow Latossol and Red Latossol, while at 4 t ha^{-1} of AgroSiCa, these values were 10.75, 8.45, and 2.46 mg L^{-1}. These slight increase of Al_T could be due to the fluoride addition to soil by AgroSiCa, that can increase the Al concentration by complexation of exchangeable Al and bringing it into soil solution (Elrashidi and Lindsay, 1986) and substitution of OH by F at the surface of amorphous aluminum oxides by ligand exchange (Huang and Jackson, 1965; Perrott et al., 1976). It is important to know that only the total aluminum levels are not sufficient to evaluate the toxicity of Al, since it is found in many species in the soil solution, and some of these species are considered non-toxic to plants. Therefore, Al_L is the one that more accurately indicates the toxicity level of the element (Boudot et al., 1996).

Decreases of Al_L levels were observed in all soils studied with the application of AgroSiCa, showing more pronounced effect at 0-10 cm depth (Fig. 1). It was observed that approximately 87, 81, 60 % of the Al_T in the soils solutions of Cambissol, Red Yellow Latossol and Red Latossol, respectively, are in the labile form and likely to be absorbed by plants. Several authors found similar results, in which most of the Al_T found in soil solution was in the form considered most toxic (Alvarez et al., 1993; Boudot et al., 2000; David and Driscoll, 1984; Perez et al., 2005; Ross and Walna et al., 2005; Tanskanen et al., 2004; Vieira et al., 2008). In the 30-40 cm layer, these percentages were 89, 85, 79%, respectively, for Cambissol, Red Yellow Latossol and Red Latossol. Despite the Al_L values of Cambissol and Red Yellow Latossol being practically the same, these percentages increased in soil with higher clay content. In other words, clayey soil showed higher levels of Al_L in the deeper layer under non AgroSiCa application due to the positive correlation between clay and organic matter. Additionally, the organic matter can influence the reduction of Al_L contents in the upper layers of these soils, since the organic material can form complexes with Al, making it less toxic and reducing the amounts of labile Al detected by the method (Lima et al, 2007; Van Hees et al., 2000; Vieira et al., 2008; Wagai et al., 2013).

The application of 4 t ha^{-1} of AgroSiCa reduced the Al labile levels in 0-10 cm depth, which represented a reduction of 83, 78 and 67%, respectively, for Cambissol, Red Yellow Latossol and Red Latossol. This reduction is because AgroSiCa contains fluoride and silicon, which are elements that can increase the soil pH, and also reduce the Al toxicity by forming complexes with less toxic. Thus, the silicon dissolution promotes the release of a hydroxyl (OH^-), neutralizing H^+ and increasing the soil pH, as observed elsewhere (Baylis et al., 1994; Barcelo et al., 1993; Camargo et al., 2007). In addition, some studies have also indicated that fluoride addition can increase soil pH due to the displacement of OH^- from clay adsorption sites or Al-OH species by F^- (Wenzel and Blum, 1992). Bond et al. (1995) found that flouride caused large decrease of Al in both the solution and exchange phases, as well as largest effect on the increase of pH. In fact, AgroSiCa may have increased soil pH, since it has a basic character and due to the release of OH^- from Fe and Al oxides/hydroxides, and also from the surface of clay minerals due to fluoride adsorption (McBride, 1994), a process that involves ligand exchange with a coordinated OH group (Omueti and Jones, 1977).

In 30-40 cm depth, the AgroSiCa reduced Al-Labile levels from 8,28 to 6,98 mg L^{-1} for Cambissol, from 6,27 to 4,32 mg L^{-1} for Red Yellow Latossol, and from 1,58 to 1,38 for Red Latossol, which means a reduction of 16, 31, and 13%, respectively, compared to non AgroSiCa application, showing that the application of this product can also reduce the Al_L content in the deeper layers, mainly in sandy soils with lowest sorption capacity, as observed for Red Yellow Latossol.

This result is relevant, since it supports the beneficial agricultural use of the AgroSiCa formed after the neutralization reaction of hexafluorosilicic acid with calcium oxide, especially when it is applied in tropical soils that are weathered and highly saturated with Al^{3+}. The chemical behavior of Al and F in soil ecosystems has been paid attention because the Al^{3+} can be complexed with the fluoride ion (F^-) in soil solution of acidic soils ($pH < 6.0$) (Xie et al., 1999). Such reaction is important, because Al complexed with ligands such as F^- is considered less toxic to plants (Whitten and Ritchie, 1991).

As the non-labile aluminum was determined by the difference between the levels of Al_T and Al_L, and we know that Al_L concentrations decreased with the application of AgroSiCa, we have as a consequence applying the product, the increase in non-labile aluminum concentrations, showing that the aluminum tends to be complexed forms and less toxic to plants at a dose of 4 t ha^{-1} AgroSiCa.

The Figure 3 shows the changes in the P fractions in soils studied in function of the doses of AgroSiCa.

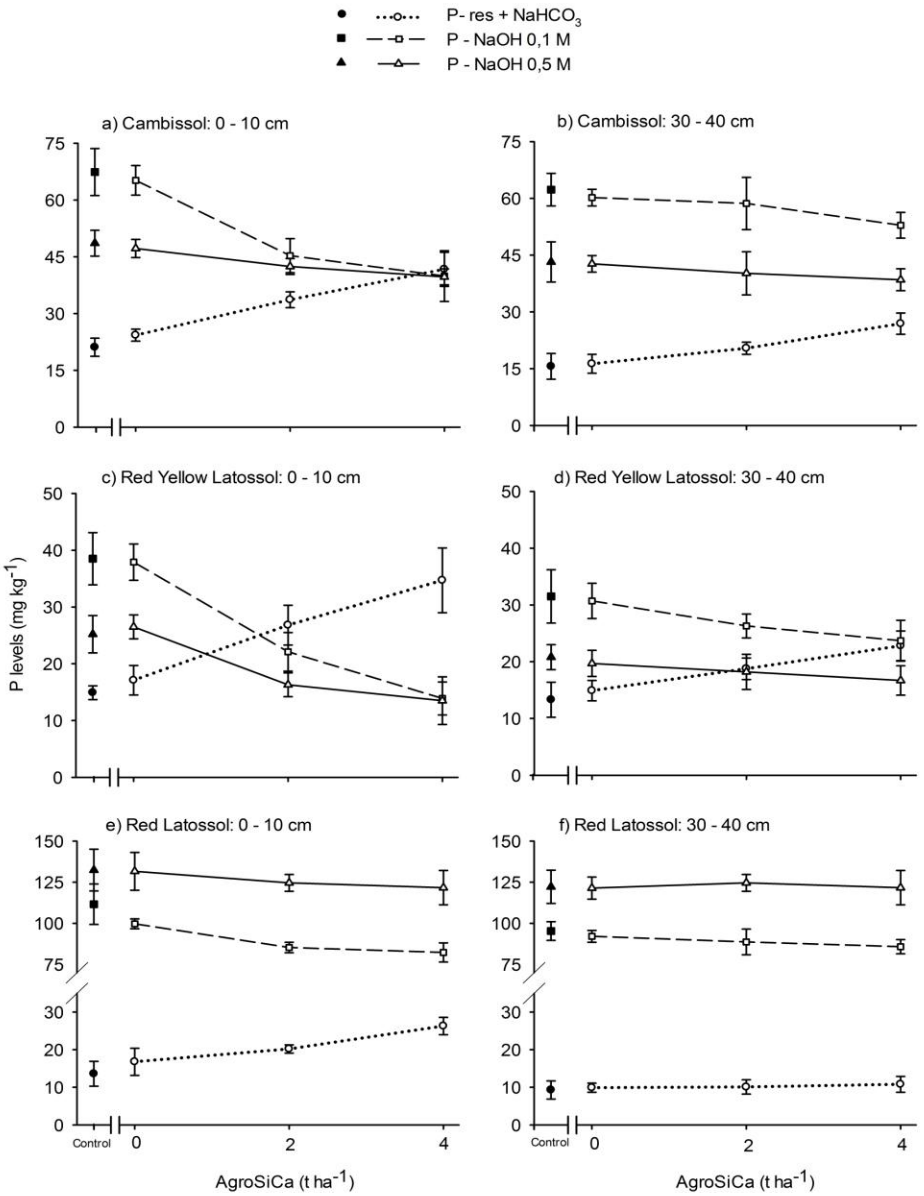

Fig 3. Levels of Fractions of P in according to the doses of AgroSiCa.

There was an increase of P fraction extracted by P res + $NaHCO_3$ in all soils studied with the application of AgroSiCa. It is worth remembering that this is the fraction of P considered labile and more available to plants. The content of this fraction observed in the control treatment were 21.1, 14.9 and 13.6 mg L^{-1} for CX, and LVAd LVd respectively. In the dose of 2 t ha^{-1} AgroSiCa these levels increased to 33.65, 26.8 and 20.2 mg L^{-1} and the dose of 4 t ha^{-1} for 41.7, 34.7 and 26.3 mg L^{-1}, considering the values of the layer 0 - 10 cm of soil where the product effect was more eminent. This increase of available P in all soils treated with AgroSiCa may be related to phosphate-silicate and phosphate-fluoride competition for sorption sites. The AgroSiCa containing Si and F was previously applied to phosphorus fertilization, thus these elements may have been adsorbed at P sorption sites, increasing the efficiency of phosphorus fertilization, since the P solubilized from the fertilizer tends to stay the most labile forms. Additionally, the P sorption sites on the soil are partially occupied, facilitating the movement of P to the soil solution and the uptake this nutrient by plants (Valle et al., 2016).

Keerthisinghe et al., 1991 studying the effects of fluoride in acid soils found positive interactions between fluoride levels, doses of P, and plant growth. The authors observed that the application of NaF improves soil acidity conditions, reducing the toxic contents of Al and increasing the efficiency of use of P by plants. Also is well established that phosphate and silicate ions are adsorbed by iron and aluminum oxides, with silicate being able to displace the previously adsorbed phosphate from oxidic surfaces. The chemical similarity of the two anionic forms is largely responsible for this behavior (McKeague and Cline, 1963). In fact, application of silicate previously to phosphate favors the bioavailability of P in highly weathered soils (Pozza et al., 2007). In addition to silicate, fluoride is also known to be able to replace phosphate on positive charges of oxidic soils (Zhang and Yu, 1997).

Modern agriculture is based on the use of substantial quantities of phosphates for both crop farming and animal husbandry (Scholz et al., 2013). Given that the sources of phosphorus are finite and more than 80% of total consumption of phosphorus in the world due to fertilizer production (Shinh et al., 2012), the most efficient use of such a fertilizer is of utmost importance. In this sense, the results of this study show that AgroSiCa can be an important product in order to increase the efficiency of phosphate fertilizers, thus minimizing the consumption of finite phosphorus sources.

Already the P fractions were extracted with 0.1 M NaOH and 0.5 M was observed that they were higher in the treatments without AgroSiCa application, which indicates that P tends to be less labile to treatments without applying this product. Wright & Coleman, 1999 report that the lowest accumulation of P in the more labile fractions is expected, especially in clay soils and more weathered with high levels of oxides and high-capacity of P sorption.

At 30-40 cm depth, at dose of 2 and 4 t ha-1 of AgroSiCa, changes were also observed in P fractions on Cambissol and Red Yellow Latossol, however in smaller proportions. These changes are due to the fact that fluoride tends to be retained in the upper soil layers in tropical soils (Cronin et al., 2000), and the effect of the AgroSiCa on the deeper layers is a consequence mainly of Si, that reaches these layers, once is more mobile in the soil than fluoride. In Red Latossol (that have greater sorption capacity, therefore less mobile Si), there were no effects of AgroSiCa in 30-40 cm layer.

4 **CONCLUSIONS**

The AgroSiCa application (product of phosphoric acid production wet process - derived from the mixture of hexafluorosilicic acid with calcium oxide) provided a reduction of labile aluminum content in the solution of all soils, with more pronounced effect in the layers of 0-10 cm. As a result non-labile aluminum levels were increased with the application of the product. There also was an increase of P fraction extracted by Resin + $NaHCO_3$ in all soils studied with application of AgroSiCa showing that the product can increase the efficiency of phosphorus fertilization and contribute to a more rational use of phosphorus sources. Already the P fractions were extracted with 0.1 M NaOH and 0.5 M was observed that they were higher in the treatments without AgroSiCa application.

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