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DESSULFURIZAÇÃO, REDUÇÃO DO POTENCIAL DE GERAÇÃO DE DRENAGEM ÁCIDA E APROVEITAMENTO EM SOLOS FABRICADOS DOS REJEITOS DE CARVÃO MINERAL DA REGIÃO CARBONÍFERA DE SANTA CATARINA

Jéssica Weiler

Tese de Doutorado

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Trabalho realizado no Laboratório de Tecnologia Mineral e Ambiental (LTM) da Escola de Engenharia da UFRGS, dentro do Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais (PPGE3M), como parte dos requisitos para obtenção do título de Doutora em Engenharia.

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Dedico este trabalho à minha mãe (in memoriam)

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RESUMO

A mineração de carvão no Brasil ocorre no sul do país e normalmente, para obter padrões requeridos em plantas termoelétricas, o carvão ROM ("Run-of-Mine") é submetido ao processamento mineral para elevar o grau de pureza do material carbonoso. O processamento gera um rejeito rico em matéria mineral, predominantemente composto por silicatos e sulfeto de ferro. Devido ao grande volume gerado, a disposição dos rejeitos demanda grandes áreas, provoca alterações na paisagem e pode causar a geração de Drenagem Ácida de Minas (DAM). A DAM decorre de um processo de oxidação dos minerais sulfetados (principalmente a pirita – FeS_2) pela reação com o oxigênio e água. O efluente é caracterizado pela elevada acidez, alta concentração de metais e sulfatos, causando sérios problemas ambientais. No Brasil, a região sul de Santa Catarina (SC) apresenta uma grande área com solos, corpos hídricos superficiais e subterrâneos altamente impactados pela DAM. Neste contexto, o objetivo do trabalho foi investigar os benefícios da separação da pirita (método de isolamento de sulfetos) e a consequente redução no potencial de geração de acidez do material remanescente. Ainda, avaliou-se o uso da fração dessulfurizada como substrato para crescimento vegetal. O beneficiamento gravimétrico foi realizado em densidades de corte adequadas à separação da pirita dos demais minerais presentes nos rejeitos, conforme curvas de separabilidade dessimétricas obtidas. A partir disso, três artigos foram desenvolvidos com as seguintes ênfases: i) apresentar os benefícios ambientais da dessulfurização dos rejeitos de carvão para a região carbonífera de SC, considerando as camadas de carvão exploradas e o uso da fração rica em pirita; ii) avaliar os impactos da separação gravimétrica na redução do potencial de geração de DAM através de ensaios estáticos e cinéticos de predição de DAM; iii) aplicar o material remanescente como matriz mineral de um substrato para o desenvolvimento vegetal, a ser utilizado na própria recuperação de áreas degradadas da mineração. Os resultados mostram diversos benefícios que podem ser alcançados. O primeiro diz respeito ao uso da pirita como fonte de enxofre para o Brasil, uma vez que o país é deficitário nesse insumo. Considerando os dados de extração de carvão local, haveria um aumento da produção nacional de enxofre de 25% ou equivalente a 539.245 ton ano^{-1} de ácido sulfúrico. Em relação à fração dessulfurizada, houve a redução no teor de $S_{pirítico}$ de até 90% no potencial de geração de DAM, com lixiviados com menor teor de metais, sulfatos e acidez. Ainda, o reduzido teor de enxofre na fração dessulfurizada possibilitou a produção de um solo fabricado. Ao rejeito de carvão, cominuído para granulometria inferior a 2 mm, foram incorporadas dosagens pré-estabelecidas de escória de aciaria, lodo de estação de tratamento de esgoto e cinza de casca de arroz para promover condições de desenvolvimento vegetal. Experimentos indicaram resultados satisfatórios para a espécie *Megathyrsus maximus var. maximus* (Guinea grass), com transformação nas formas do enxofre e redução de 50% do $S_{pirítico}$ após o plantio. Pode-se concluir que o processo de dessulfurização dos rejeitos de carvão proporciona o aproveitamento de materiais e a redução de impactos ambientais, criando alternativas de diversificação de atividades para o setor carbonífero. Isso é consistente com o princípio de sustentabilidade no gerenciamento de resíduos, conservação de recursos naturais e o conceito de economia circular.

Palavras-chaves: processamento de rejeitos; isolamento de sulfetos; pirita; tecnossolos; aproveitamento de resíduos.

ABSTRACT

Coal mining in Brazil occurs in south of the country and generally, to obtain standards required in thermoelectric plants, ROM (Run-of-Mine) coal is submitted to mineral processing to increase the purity of the carbonaceous material. The processing generates a waste rich in mineral material, mostly composed of silicates and iron sulfide. Due to the considerable amount produced, the disposal of the coal wastes demand large areas, causes landscape and topography modifications and can produce the Acid Mine Drainage (AMD). AMD results from an oxidation process of sulfide minerals (mainly pyrite - FeS_2) by reaction with oxygen and water. The effluent is characterized by high acidity, high concentration of metals and sulfates, which can result in serious environmental problems where it occurs. In Brazil, the southern region of Santa Catarina has a large area with soils, surface and groundwater severely contaminated by AMD. In this context, the present study investigates the benefits of pyrite separation (sulfide isolation method), resulting in a reduction of the acidity generation potential of much of the discarded material. Still, the use of the desulfurized fraction as a substrate for plant growth was evaluated. The beneficiation was performed by gravimetric procedure in cutting densities to obtain satisfactory separation of the pyrite from other minerals present in coal waste, according to desimetric separability curves. From this, three articles were developed with the following focus: i) present the environmental benefits of desulfurization of coal wastes for the SC coal region, considering the coal seams exploited and the use of pyrite fraction; ii) verify the efficiency of gravimetric separation to reduce the potential for DAM generation through static and kinetic tests of DAM prediction; and iii) use of the remaining material as a mineral matrix of a substrate for plant development, which could be used in the restauration process of degraded areas of mining. The results show several benefits that could be obtained. The first concerns the pyrite use as a source of sulfur for Brazil, since the country is deficient in this element. Considering the local extraction data, there would be an increase in sulfur national production of 25% or equivalent to 539,245 tons year^{-1} of sulfuric acid. Regarding desulfurization, there was a reduction in the $S_{piritic}$ content and up to 90% in the potential for AMD generating, and leachate with a lower content of metals, sulfates and acidity. Furthermore, the low sulfur content in the desulfurized fraction made it possible to produce a soil-like substrate. The material was comminuted to a particle size of less than 2 mm and then, incorporated pre-established dosages of steel slag, sewage treatment plant sludge and rice husk ash to promote plant development. The experiment indicated satisfactory results for the species *Megathyrsus maximus var. maximus* (Guinea grass), with transformation in the forms of sulfur and 50% reduction in Spiritic after planting. It is considered that the process of desulfurization of coal wastes provides the use of materials and the reduction of environmental impacts, creating alternatives to diversify activities for the coal sector. This is consistent with the principle of sustainability, waste management, conservation of natural resources and the concept of circular economy.

Key-words: wastes processing; sulfide removal; pyrite; technosols; waste recovery.

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ABA: Contabilização de Ácidos e Bases

ABCM: Associação Brasileira de Carvão Mineral

ABNT: Associação Brasileira de Normas Técnicas

AP: Potencial de Acidez

ASTM: American Society for Testing and Materials

BB: Camada Barro Branco

BO: Camada Bonito

CETEM: Centro de Tencologia Mineral

DAM: Drenagem Ácida de Minas

DNPM: Departamento Nacional de Produção Mineral

EPA: Environmental Protection Agency

ISO: International Organization for Standardization

LTM: Laboratório de Tecnologia Mineral e Ambiental

NBR: Norma Brasileira Registrada

NNP: Potencial de Neutralização Líquido

NP: Potencial de neutralização

pH: Potencial Hidrogeniônico

ROM: Run-of-Mine

SIECESC: Sindicato da Indústria da Extração de Carvão do Estado de Santa Catarina

UFRGS: Universidade Federal do Rio Grande do Sul

SLS: Soil-like substrate

CW: Coal Waste

SC: Santa Catarina

RS: Rio Grande do Sul

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PARTE I

1. INTRODUÇÃO

O carvão mineral fornece um terço de toda energia usada no mundo e, mesmo com o incentivo às energias mais limpas e renováveis, estima-se que o uso de carvão continue significativamente alto no futuro (IEA, 2018). Em função disso, é fundamental a aplicação de conceitos sustentáveis e uso de tecnologias para reduzir os impactos relacionados à atividade, mantendo-a ambientalmente competitiva (Anawar, 2015; Franks et al., 2011; Si et al., 2010).

Os impactos ambientais da mineração de carvão ocorrem tanto nos processos de extração mineral como de beneficiamento. No processo de extração pode ocorrer a degradação da paisagem, desconfiguração topográfica, subsidência de terreno, alteração de níveis freáticos, erosão e assoreamento (Bell et al., 2001; Feng et al., 2019,). No beneficiamento mineral, há necessidade de estruturas para a disposição dos rejeitos, com riscos de geração de efluentes ácidos e de contaminação de corpos hídricos e solo (Bian et al., 2009, Komnitsas et al., 2001, Kopezinski, 2000).

Em relação ao beneficiamento mineral, este é realizado a fim de aumentar a pureza do material carbonoso, eliminando parte do material inorgânico associado ao carvão ROM ("Run-of-Mine"). As rochas que compõe o rejeito ao final do processo são argilitos, folhelhos, siltitos, arenitos, e, muitas vezes, ocorre presença de sulfetos de ferro (como a pirita – FeS_2). O volume de rejeito gerado varia muito com as características geológicas do local de exploração, método de lavra e eficiência do beneficiamento (Leonard, 1991).

No Brasil, a mineração ocorre no sul do país, e as reservas estão localizadas nos Estados do Rio Grande do Sul, Santa Catarina e Paraná, com produção de carvão energético equivalente a 56,3%, 41,2% 2,5%, respectivamente (ABCM, 2018). O carvão extraído nesses estados varia de qualidade, havendo, do sul para o norte, um aumento no teor de enxofre (Chaves, 2008). Especificamente na região sul de Santa Catarina, os rejeitos correspondem a 2/3 da massa de material extraído, com teor aproximado de 11% de pirita (Amaral Filho et al., 2013). As camadas de carvão mais exploradas nessa região são a Barro Branco e Bonito, e o método de extração predominante é lavra subterrânea por "câmaras e pilares". A lavra subterrânea minimiza a movimentação de rocha para a extração do carvão, entretanto, devido a questões de segurança e logística de produção, o uso dos rejeitos como "backfill" ainda não é realizado de forma ampla na região, sendo dispostos predominantemente em módulos de rejeitos em superfície (Koppe e Costa, 2008).

Os módulos de rejeitos são considerados passivos ambientais porque ocupam grandes áreas, modificam a paisagem e, devido à presença de minerais sulfetados, podem gerar Drenagem Ácida de Minas (DAM), um dos maiores problemas ambientais enfrentados pela indústria da mineração (Simate e Ndlovu, 2014; Skousen et al., 2019).

A DAM é gerada pela reação dos minerais sulfetos (principalmente a pirita) com água e oxigênio. As reações de oxidação da pirita (FeS_2) liberam íons H^+, Fe^{2+}, Fe^{3+} e sulfatos (SO_4^{2-}) formando uma drenagem com alta acidez e elevada concentração de ferro e sulfato. O baixo pH da drenagem também permite a dissolução de outros metais que podem estar associados aos rejeitos, tais como alumínio (Al), manganês (Mn), zinco (Zn), chumbo (Pb), cádmio (Cd), cobre (Cu), arsênio (As) e selênio (Se) (Akcil e Koldas, 2006; Johnson e Hallberg, 2005). Ainda, as reações podem ser intensificadas quando há presença de bactérias da espécie *Acidithiobacillus ferrooxidans*, pois estas têm capacidade de oxidar em meio ácido os íons Fe^{2+} à Fe^{3+} (Baker e Banfield, 2003; Kontopoulos, 1998). As reações de DAM, uma vez iniciadas, são de difícil controle e podem durar por dezenas e até centenas de anos.

Diversos métodos de controle podem ser aplicados se os rejeitos tiverem potencial de formação de DAM. Eles podem ser preventivos (evitando ou reduzindo a geração da DAM), ou remediativos (aplicando tratamentos após a sua geração). Os métodos preventivos, tais como isolamento de sulfetos, mistura com materiais alcalinos e aplicação de coberturas secas, evitam que os problemas relacionados à DAM sejam gerados, e teoricamente são preferíveis aos métodos remediativos. Entretanto, o tratamento químico ativo da DAM, utilizando reagente alcalinos para elevar o pH e precipitar os metais, ainda é o mais utilizado pelo setor mineral para controle da DAM (Skousen et al., 2019).

A prática de construção de módulos de rejeitos e tratamento ativo da DAM é oneroso e insustentável a longo prazo. Modelos de previsão de DAM em depósitos de rejeitos da mineração mostram resultados alarmantes. No norte de Hokkaido, Japão, estudos realizados para uma mina de cobre e zinco mostraram que, mesmo após 40 anos de exposição ao meio ambiente, os rejeitos ainda contêm pirita (FeS_2), com previsão de até 1000 anos de geração de efluente que necessita tratamento para alcançar padrões de lançamento (Sasaki e

Igarashi, 2013; Tabelin et al. 2018). Em SC, a previsão realizada em apenas um módulo de rejeitos de carvão, que possui mais de 14 Mt de rejeito, foi de 600 anos (Weiler et al., 2016).

Na região carbonífera de SC, durante muitos anos, os rejeitos foram dispostos de forma imprópria e sem tratamento da DAM. Isso resultou em contaminação de solos e corpos hídricos superficiais e subterrâneos, com aproximadamente 6000 ha de áreas severamente degradadas, e 1200 km de trechos de rios, correspondendo a 6% das bacias hidrográficas dos rios Araranguá, Urussanga e Tubarão (Brasil, 2016; Romano Neto et al., 2017). Hoje, a recuperação do passivo é tratada por Ação Civil Pública com as mineradoras locais, o que está atenuando gradativamente os efeitos da DAM, mas muitas áreas são "órfãs" e continuam impactando o meio ambiente (Rocha-Nicoleite et al., 2017).

Considerando as questões relacionadas à disposição de rejeitos e geração de DAM, e toda problemática ambiental exemplificada em SC, estudos vêm sendo conduzidos visando o uso de métodos preventivos para evitar a geração de DAM. Amaral Filho (2014) e Weiler et al. (2016) utilizaram o método de isolamento de sulfetos por meio denso para separar a fração pirítica e, consequentemente, reduzir o potencial de geração de DAM do rejeito. Foi realizada a separação gravimétrica do rejeito em três frações, de acordo com densidade dos minerais presentes: (i) uma fração leve, com significante teor de carbono, a qual poderia ser utilizada para geração de energia; (ii) uma fração com maior densidade devido ao alto teor de pirita, com diversos usos potenciais; e (iii) uma fração intermediária, com maior teor de cinzas, menor teor de enxofre e reduzido potencial de geração de acidez, que poderia ser disposta com menores riscos ao meio ambiente.

Em relação à fração pirítica, já se apresentaram possibilidades de aproveitamento na produção de sulfato férrico (Colling, 2014; Menezes, 2009), sulfato ferroso (Vigânico, 2014) e pigmentos à base de óxidos de ferro como a hematita (vermelho), goetita (amarelo) e magnetita (preto), (Lopes, 2017; Silva, 2010). Para a fração intermediária, o material foi considerado inerte (Weiler, 2014) e mostrou potencial aplicação na construção civil (Santos, 2012) e tecnossolos (Firpo, 2015).

Os tecnossolos compreendem solos com influência antrópica cujas propriedades e gênese tem origem em materiais não naturais (tais como resíduos domésticos, lodos, resíduos da construção civil, indústria e mineração) (IUSS Working Group WRB, 2014). A possibilidade de uso dos rejeitos dessulfurizados como matriz mineral de um tecnossolo foi sugerida por Firpo, 2015 e Firpo et al., 2015. Esses rejeitos, quando misturados a outros materiais condicionantes de solo para ajuste de pH, matéria orgânica e nutrientes, mostrou crescimento vegetal satisfatório das espécies *Sorghum bicolor* e *Avena strigosa* e indicou que o substrato produzido teria potencial para o início de uma sucessão ecológica, importante na recuperação de áreas degradadas. O estudo abriu possibilidades para pesquisas considerando o uso de outros tipos de rejeitos de carvão e resíduos condicionadores de solo, diferentes espécies, análise da evolução do teor e formas de enxofre ao longo do tempo bem como aspectos microbiológicos do solo (Amaral Filho et al., 2020; Weiler et al., 2019, 2020)

O uso de tecnossolos poderia substituir a necessidade dos solos de áreas de empréstimo utilizado na recuperação de áreas degradadas, evitando a necessidade de aquisição, processos de licenciamento ambiental, e degradação de novas áreas por parte das mineradoras. Os solos são utilizados para reconformação topográfica e formação de uma camada de solo fértil, necessário à revegetação do local degradado (Singh, 2002; Sheoran et al., 2010). Dessa forma, nesses locais é importante a avalição do reestabelecimento de condições físicas, químicas e biológicas do solo, tais como agregação, compactação, níveis de matéria orgânica, fertilidade, além do monitoramento de possíveis focos de contaminação (Bolan et al., 2017; Daniels and Zipper, 2010; He et al., 2015). No Brasil, muitos estudos avaliam esses aspectos em áreas de recuperação nas regiões carboníferas (Campos et al., 2003; Citadini-Zanette et al, 2018; Costa e Zocche, 2009, Frasson et al., 2016; Leal et al., 2016; Rocha-Nicoleite et al., 2018; Stumpf et al., 2018; Stumpf et al., 2016;), destacando a importância e a necessidade da presença de solos férteis nessas áreas.

Diante do exposto, considerando a atual tendência de sustentabilidade no gerenciamento de resíduos na mineração e a problemática gerada pelas áreas degradas originadas pelos mesmos, métodos preventivos que busquem evitar a formação de drenagem ácida e a utilização dos rejeitos devem ser priorizados, evitando que os mesmos tenham disposição final em módulos. Este trabalho é baseado na utilização do método de isolamento de sulfetos aos rejeitos da região carbonífera de SC e tem como objetivo apresentar os benefícios ambientais da separação da pirita (principal geradora de acidez) e possibilidades de usos dos rejeitos. Os resultados serão apresentados em três artigos, que foram produzidos com as seguintes ênfases: o uso da pirita para produção de enxofre e ácido sulfúrico, considerando os benefícios ambientais e econômicos para a região sul de SC; a redução do potencial de geração de acidez do rejeito após a dessulfurização apresentada através de ensaios estáticos e cinéticos; e uso do material com reduzido teor de enxofre como matriz mineral de um tecnossolo, levando em consideração principalmente a transformação nas formas do enxofre.

2. JUSTIFICATIVA E INTEGRAÇÃO DOS ARTIGOS

O processamento dos rejeitos de carvão para separação da pirita é conveniente não somente por reduzir o potencial de geração de acidez do resíduo como também por possibilitar o uso da pirita e do material remanescente com reduzido teor de enxofre. Essa é uma abordagem preventiva e de valorização de rejeitos, adequada do ponto de vista sustentável e do gerenciamento dos resíduos sólidos. Neste contexto, foram desenvolvidos estudos com os rejeitos de carvão da região carbonífera de SC, uma região com histórico de impactos ambientais devido à disposição inadequada dos rejeitos e geração de DAM.

Serão apresentados a seguir três artigos relacionados ao tema:

I – Weiler, J., Schneider, I.A.H., 2019. Pyrite utilization in the carboniferous region of Santa Catarina, Brazil - Potentials, challenges, and environmental advantages. REM: International Engineering Journal 72(3), 515–522.

II – Amaral Filho, J.R., Weiler, J., Broadhurst, J.L., Schneider, I.A.H., 2017. The Use of Static and Humidity Cell Tests to Assess the Effectiveness of Coal Waste Desulfurization on Acid Rock Drainage Risk. Mine Water and the Environment 36 (3), 429–435.

III – Weiler, J., Firpo, B.A., Schneider, I.A.H., 2018. Coal waste derived soil-like substrate: An opportunity for coal waste in a sustainable mineral scenario. Journal of Cleaner Production 174, 739–745.

Na Figura 1 apresenta-se esquematicamente a metodologia e a integração dos artigos que compõem o presente trabalho.

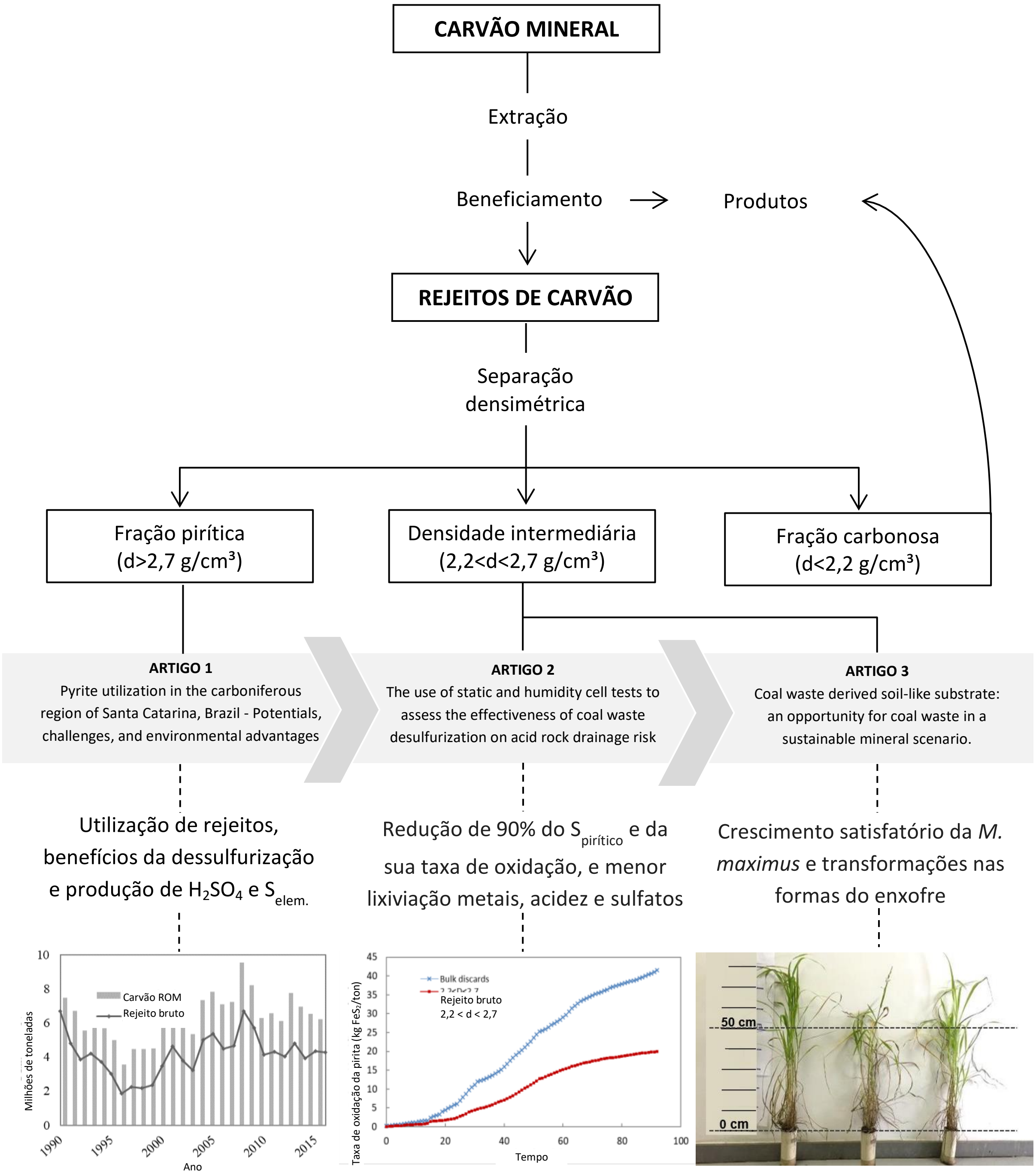

Figura 1. Esquema metodológico utilizado para o desenvolvimento do trabalho.

O artigo 1 apresenta resultados de estudos de separabilidade gravimétrica do rejeito e utilização da fração pirítica das duas principais camadas de carvão exploradas na região carbonífera de SC, a camada Barro Branco (BB) e Bonito (BO). Curvas densimétricas e a separação gravimétrica com meios densos (utilizando líquidos orgânicos) nos cortes de 2,2 e 2,7 foram realizadas para obtenção de três frações: d < 2,2 g cm^{-3} (fração carbonosa), 2,2 < d < 2,7 g cm^{-3} (fração dessulfurizada), d > 2,7 g cm^{-3} (fração pirítica). Compararam-se ambas as camadas (BB e BO) em termos de facilidade de dessulfurização e também a questão do uso da pirita para produção de ácido sulfúrico, com os benefícios ambientais gerados a partir da redução no potencial de geração de acidez dos rejeitos. Os resultados mostraram que a camada BB possui maior facilidade para separação por meio denso quando comparada a camada BO. Isso ocorre devido a diferentes perfis litológicos das camadas: a camada BB é mais estreita e homogênea, enquanto a BO é mais espessa e estratificada, intercalando-se com siltito e arenito. Isso resulta em algumas vantagens para a BB, considerando o método de separação gravimétrica nas densidades aplicadas nesse estudo: menor teor de enxofre na fração energética ($d < 2,2$ g cm^{-3}) e intermediária ($2,2 < d < 2,7$ g cm^{-3}) e maior teor de enxofre na fração pirítica ($d > 2,7$ g cm^{-3}). Comparado ao rejeito bruto, a redução do potencial de geração de acidez do rejeito intermediário (dessulfurizado) foi de 90% na camada BB, enquanto que para a camada BO a redução foi de 65%. A partir dessa constatação, apresentaram-se dados da tendência de aumento da exploração da camada BO devido ao esgotamento da BB e, consequentemente, maiores desafios do ponto de vista de processamento de rejeitos. Considerando a aplicação da fração pirítica, com teor médio de pirita de 58,2%, os rejeitos apresentaram potencial para uso como matéria prima na produção de enxofre e ácido sulfúrico. O estudo mostrou que, embora as camadas apresentem diferenças quanto a facilidade de separação por meio denso, há vantagens ambientais pela redução da geração de acidez e benefícios econômicos pelo uso da pirita.

Destaca-se que no artigo 1 foram apresentados resultados para os rejeitos provenientes da jigagem, circuito de grossos, com partículas de diâmetro entre 2 e 50.8 mm. Entretanto, as considerações sobre o uso da pirita foram feitas para toda a massa de rejeitos gerada na região carbonífera de SC, incluindo a massa de finos ($d < 2$ mm), uma vez que estudos desenvolvidos anteriormente apresentam comportamento similar nos ensaios de afunda-flutua para ambas as granulometrias (Weiler, 2016).

O artigo 2 apresenta as características do rejeito gerados no beneficiamento de carvão mineral, circuito de grossos da camada Barro Branco - SC. Esses rejeitos foram submetidos à separação gravimétrica utilizando meio denso de Fe-Si em escala laboratorial, nas mesmas densidades de cortes do estudo anterior. Testes estáticos e cinéticos de predição de DAM foram realizados no rejeito bruto e na fração dessulfurizada, com objetivo de avaliar a eficiência da dessulfurização. Devido a redução do teor de enxofre pirítico, houve uma redução de quase 90% no potencial de geração de acidez dos rejeitos, considerando ensaios estáticos. O ensaio cinético realizado em células úmidas durante 92 semanas também apresentou resultado satisfatório: os lixiviados do rejeito dessulfurizado apresentaram redução de Fe (60%), Al (54%), Zn (48%), sulfato (51%) e acidez (55%), quando comparados ao rejeito bruto. Em termos de oxidação da pirita, a taxa de oxidação no período do estudo foi o dobro para o rejeito bruto (64 g FeS_2 t^{-1} dia^{-1}) sendo consumido apenas 31% do S presente, enquanto que para o rejeito processado (32 g FeS_2 t^{-1} dia^{-1}), 98% do S foi consumido. O estudo demonstrou que se o meio denso fosse aplicado aos rejeitos para dessulfurização antes da disposição final dos mesmos, haveria redução em termos de taxa de oxidação da pirita e melhora nos parâmetros de qualidade da drenagem. Isso facilitaria o tratamento e diminuiria o tempo de geração da DAM nos módulos de rejeitos, implicando em redução de custos e riscos ambientais em longo prazo.

A partir dos resultados obtidos nos estudos anteriores, percebeu-se que grande parte do rejeito representa a fração dessulfurizada e que, embora essa possua menores riscos ambientais, poderia ser considerada para outra aplicação. Além disso, existe uma grande demanda de uso de solos para recuperação de áreas degradadas da mineração. Essa problemática foi considerada um terceiro estudo (artigo 3). A fração dessulfurizada foi utilizada como matriz mineral em substratos para crescimento vegetal, no caso um tecnossolos, que poderia ser utilizado para recuperação das próprias áreas mineradas. O substrato foi produzido a partir da fração intermediária do rejeito da camada Barro Branco, escória de aciaria (alcalinizante da acidez residual), lodo de estação de tratamento de esgoto (fonte de matéria orgânica e nutrientes), cinza de casca de arroz (para auxiliar na estrutura física). O estudo considerou a avaliação do crescimento vegetal com *Megathyrsus maximus* (Guinea grass), especiação do enxofre (pirítico, sulfático e orgânico) e alterações nos parâmetros de geração de acidez dos rejeitos após plantio. O sistema mostrou uma redução de 50% no teor de enxofre pirítico, com aumento da forma orgânica e sulfática, coerente com a exposição do material ao meio oxidante, atividade microbiana do solo e ação das raízes. A produção de acidez do rejeito foi contrabalançada pelo material neutralizante. O crescimento vegetal e os parâmetros de fertilidade foram considerados adequados. O estudo, além de limitar os impactos associados à disposição de resíduos de carvão, incorpora outros resíduos sólidos e pode ser uma alternativa em áreas de recuperação da mineração.

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PARTE II

3. PYRITE UTILIZATION IN THE CARBONIFEROUS REGION OF SANTA CATARINA, BRAZIL - POTENTIALS, CHALLENGES, AND ENVIRONMENTAL ADVANTAGES

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Pyrite utilization in the carboniferous region of Santa Catarina, Brazil - Potentials, challenges, and environmental advantages

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Abstract

The main coal seams explored in the coal region of Santa Catarina are Barro Branco (BB) and Bonito (BO). Owing to the association with the mineral matter, the tailings generated in the beneficiation are arranged in disposal areas, and subject to the generation of acid mine drainage (AMD). The objective of this study was to evaluate the use of pyrite present in the coal rejects of the BB and BO seams and the environmental gains with desulfurization. For this purpose, densimetric separability test, ash, sulfur, and AMD generation analyses were performed. In addition, the amount of pyritic concentrates and sulfuric acid were estimated considering the current level of production. Three densimetric fractions were obtained: less than 2.2 (energetic material), between 2.2 and 2.7 (low sulfur material), and greater than 2.7 g cm^{-3} (pyrite concentrate). The results revealed that the two seams could be beneficiated by gravimetric processes, obtaining pyrite concentrates with approximately 60% pyrite. By converting pyrite to sulfuric acid would represent an increase of 500,000 tons per year in the Brazilian production of this material and, in environmental terms, a reduction of up to 90% of the acidity potential to be disposed in the environment in the case of the BB seam and 65% for the BO seam. It was also observed that the “desulfurized” fraction of the BO had higher levels of pyrite and a higher potential for acidity generation than the BB seam, implying greater risks of environmental contamination and higher acid water treatment costs.

Keywords: pyrite, coal waste, desulfurization, waste recovery, environment.

Introduction

The coal-producing region of Santa Catarina, Brazil, supplies the Jorge Lacerda thermoelectric complex, the largest thermoelectric plant in South America with an installed capacity of 852 MW (Kalkreuth et al., 2010). In this region, the Barro Branco, Bonito and, to a lesser extent, the Irapuá (I) seams are commercially exploited. Historically, the Barro Branco (BB) seam was the most exploited. However, with the depletion of many of the mines in recent years, production has also turned to the Bonito (BO) seam. Thus, it is important that studies should be conducted aiming at the environmental aspects of both seams. Figure 2 contextualizes the Santa Catarina coal region, presenting the stratigraphic profile of the region and details of the BB and BO seams.

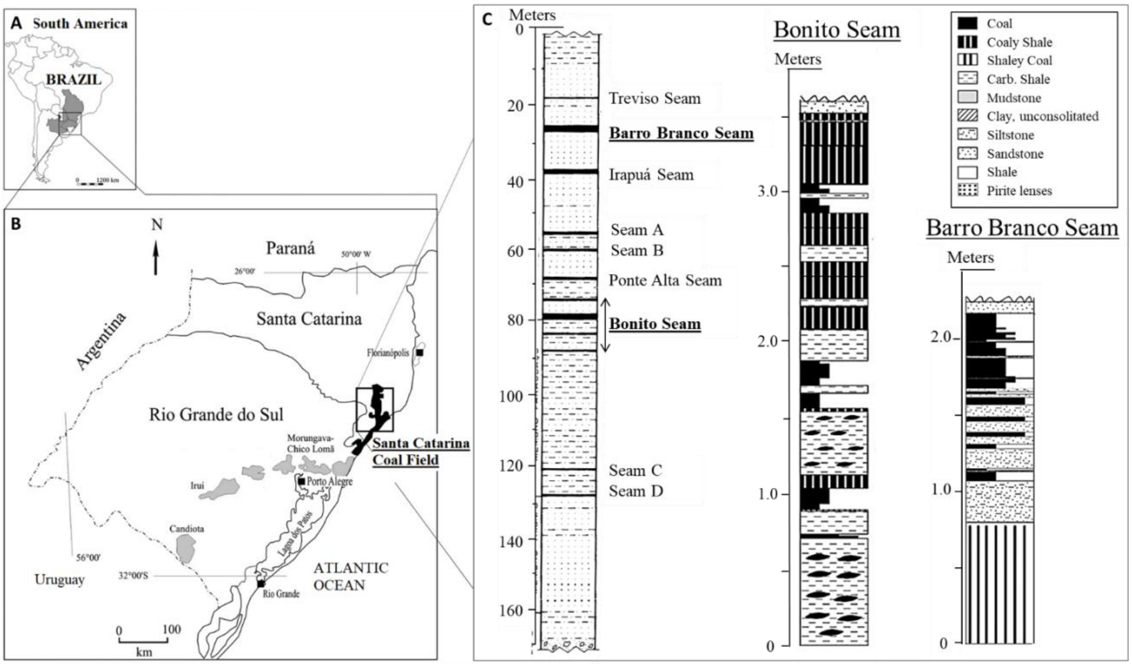

Figure 2. (A) Location of the southern Paraná Basin, Brazil; (B) Distribution of major coalfields in Rio Grande do Sul and Santa Catarina States; (C) Transect showing lithological profile in Santa Catarina Coalfield and highlight of the Bonito and Barro Branco seams. Modified from Kalkreuth et al. (2010).

The extraction of these layers is performed predominantly by underground mining and, due to mechanization, intercalation with sedimentary rocks (shales, siltstones, and sandstones), and the presence of pyrite nodules (iron sulfide - FeS_2), the run-of-mine (ROM) coal should be processed to meet the combustion standards. The coal beneficiation plants discard approximately 65% of the mass of the ROM. These discarded materials have a sulfur content close to 6%, corresponding to 11.2% of pyrite (Amaral Filho et al., 2013). It is estimated that about 320 million tons of coal wastes has already been produced in Santa Catarina (SIECESC, 2017). Figure 3 presents data on the production of ROM coal and the amount of coal rejects generated during the beneficiation phase between 1990 and 2016.

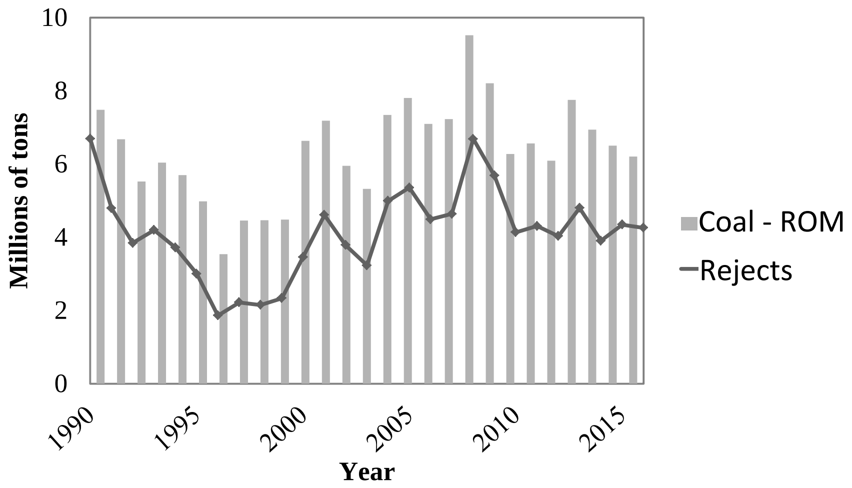

Figure 3. Coal (run of mine) and reject production in the coal region of Santa Caterina between the years 1990 and 2016 (SIECESC, 2017).

The wastes that were disposed improperly and left untreated for many years generate acid rock drainage (ARD), contaminating soils, as well as surface and underground water resources. In this region, it is estimated that 6000 ha were severely degraded, reaching 1200 km of river stretches, corresponding to 6.1% of the Araranguá, Urussanga, and Tubarão basins (Brasil, 2016; Romano Neto et al., 2017). Currently, the recovery of liabilities is being handled by a Public Civil Action with local mining companies, which is gradually mitigating the ARD effects, but many areas are abandoned and continue to impact the environment (Rocha-Nicoleite et al., 2017).

Even with all the environmental problems, the coal industry does not apply techniques that aim at the recovery of the products contained in the tailings. Separation of pyrite would allow it to be used for various products, such as sulfuric acid, avoiding considerable environmental impact and adding value to the mineral coal production chain.

The production of sulfuric acid from pyrite is achieved by roasting: heating the material at temperatures from 600 to 1000°C in an oxidizing environment (addition of air) and transforming them into gaseous sulfur dioxide. Subsequently, sulfur dioxide is oxidized to sulfur trioxide and then hydrolyzed to sulfuric acid. This well-established technology is used worldwide (ESA/EFMA, 2000; Chepushtanova and Luganov, 2007; Runkel and Sturm, 2009; Ashar and Golwalkar, 2013).

The objective of this study was to measure the production of pyrite concentrates and their potential in terms of sulfuric acid conversion from the current coal exploration scale of the BB and BO seams. In addition, we evaluated the reduction of the acidity potential of the remaining material, with lower pyrite content. The results of the two seams were compared, considering the generation of coal wastes and environmental risks in the region of study.

Material and methods

Coal tailings samples were obtained during the jigging stage, coarse circuit (with grain size between 2.0 and 50.8 mm), from the coal beneficiation processes for the BB and BO seams, located in the coal region of Santa Catarina. In both samples, the coarse fraction was selected because it contributes to more than 70% of the discarded mass. Sampling was conducted by the mining companies, and the procedure consisted in taking samples of approximately 10 kg twice a day during 1 month, numbering approximately 300 kg, which was sent to the experimental site. At the laboratory, after sun drying and homogenization, the samples were properly divided with a Jones Riffle splitter for the experimental work.

The washability test (float/sink) was carried out according to ASTM D4371-06 (ASTM, 2012a). The densities used were 1.7, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, and 2.7 g cm^{-3}. The preparation of dense medium was performed by mixing dense organic tribromomethane ($CHBr_3$), having a density of 2.81 g cm^{-3}, and tetrachlorethylene (C_2Cl_4), having a density of 1.62 g cm^{-3}. The liquids were mixed to the desired density that was measured using a densimeter. Each fraction obtained in the densimetric tests was submitted to ash and total sulfur analyses.

From the washability test, the densimetric separability curves were constructed for ash and sulfur contents, as was the Near Gravity Material (NGM) curve (Leonard, 1979; Tavares and Sampaio, 2005). The analysis of the densimetric separability curves allowed dividing the two samples (BB and BO) into three distinct densimetric fractions: fraction with a density less than 2.2 g cm^{-3} (energetic material, $d < 2.2$), fraction with an average density between 2.2 and 2.7 g cm^3 (material with reduced sulfur, $2.2 < d < 2.7$), and fraction with a density greater than 2.7 g cm^3 (pyritic concentrate, $d > 2.7$).

The ash analysis was performed by a gravimetric procedure according to ASTM D3174-12 (ASTM, 2012b). The total sulfur analysis (S_{total}) was conducted by using instrumentation in a Leco SC 457 device. Sulfur forms ($S_{pyritic}$ and $S_{sulfate}$) were analyzed by titration procedures according to ASTM D2492-02 (ASTM, 2012c). The value of the organic sulfur was calculated by the difference of the total sulfur concentration and the sum of the sulfate and pyritic sulfur. The values of ash and sulfur analyses, on a wet basis, were corrected for a dry basis according to ASTM D3173-11 (ASTM, 2011).

The information obtained from the pyritic concentrate was used to estimate the production of sulfuric acid in the region. For this purpose, the following were used: data of coal production and coal wastes generation in Santa Catarina provided by SIECESC (2017), production data/consumption of S in Brazil published in the Mineral Summary 2014 (DNPM, 2016), and molar ratios of the pyrite roasting reactions for the formation of sulfuric acid.

The thermal treatment of pyrite (FeS_2) in the presence of air current produces ferric oxide (Fe_2O_3) and sulfur dioxide (SO_2) (Eq. (1)). Sulfur dioxide is oxidized to sulfuric anhydride (SO_3) (Eq. (2)), which, by hydrolysis, is converted to sulfuric acid (H_2SO_4) (Eq. (3)). To calculate the mass ratio of pyrite required to produce sulfuric acid, the following reactions were used:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \qquad \text{Eq. (1)}$$

$$8SO_2 + 4O_2 \rightarrow 8SO_3 \qquad \text{Eq. (2)}$$

$$8SO_3 + 8H_2O \rightarrow 8H_2SO_4 \qquad \text{Eq. (3)}$$

When adding the reactions, the result is the following global equation (Eq. (4)):

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4 \qquad \text{Eq. (4)}$$

Thus, knowing the molar masses of pyrite (FeS_2 = 120 g mol^{-1}) and sulfuric acid (H_2SO_4 = 98 g mol^{-1}) and that for each 4 mol of pyrite (480 g FeS_2), produce 8 mol of acid (784 g of H_2SO_4), it is estimated that, for every 1 kg of pyrite, 1.6 kg of sulfuric acid is produced.

Finally, to compare the potential for acidic generation of the coal waste before and after pyrite removal for both seams, the samples of raw waste (before processing to remove the pyrite) and the desulfurized fraction ($2.2 < d < 2.7$) were submitted to the static acid and base accounting (ABA) test proposed by Sobek et al. (1978). The acidity generation potential (AP) was measured from the total sulfur analysis (Eq. (5)). Determination of the neutralization potential (NP) was performed by digestion of the sample with hydrochloric acid, being heated at 90°C for 1 h to consume the neutralizing minerals, followed by NaOH titration to pH 7.0 (Eq. (6)). With the AP and NP values, the liquid neutralization potential (NNP) was calculated according to Eq. (7).

$$AP\ (kgCaCO_3\,t^{-1}) = 31.25 \times \%S \qquad \text{Eq. (5)}$$

$$NP\ (kgCaCO_3\,t^{-1}) = \left(HCl_{cons.}, \frac{g}{g} sample\right)\left(\frac{50}{36.5}\right) \times \%S \qquad \text{Eq. (6)}$$

$$NNP\ (kgCaCO_3\,t^{-1}) = NP - AP \qquad \text{Eq. (7)}$$

If the difference between NP and AP is negative, then there is the potential for the residue to generate acid drainage. If it is positive, the risk is lower. Thus, the ABA criteria for identification of the acidity potential of the materials are as follows (Lapakko, 1993):

NNP < −20 kg $CaCO_3$ ton^{-1}: indicates the formation of acidity;

NNP > +20 kg $CaCO_3$ ton^{-1}: indicates that there will be no acidic formation;

−20 < NNP < +20 kg $CaCO_3$ ton^{-1}: difficult to predict its behavior, and other tests are necessary to predict the occurrence of AMD

The data obtained for the BB and BO seams were compared considering the current coal-processing scenario in the Santa Catarina region and the environmental benefits would be if the practice of pyrite concentration was adopted in the region.

Results and discussion

Figure 4 presents the washability curves and NGM of the coal waste from the BB and BO seams. From these curves, it is possible to estimate the mass corresponding to the cut density, as well as the ash and sulfur contents of the floated and immersed fractions.

The cutting densities were defined at 2.2 and 2.7 g cm^{-3}, prioritizing (a) the recovery of a carbonaceous fraction still present in the coal waste, (b) obtaining an intermediate fraction with higher mineral content and lower sulfur content, and (c) obtaining a pyrite concentrate, with more than 30% of sulfur (and, consequently, the desulfurization of the remainder of the material). The values of NGM, parameter indicating the degree of difficulty of separation of the material, were of NGM 18% at the cutting density of 2.2 g cm^{-3} and 10% at cutting density of 2.7 g cm^{-3}. In both densities, but especially in 2.7 g cm^{-3}, no major separation difficulty is expected in conventional gravimetric processing equipment (Leonard, 1991; Tavares and Sampaio, 2005).

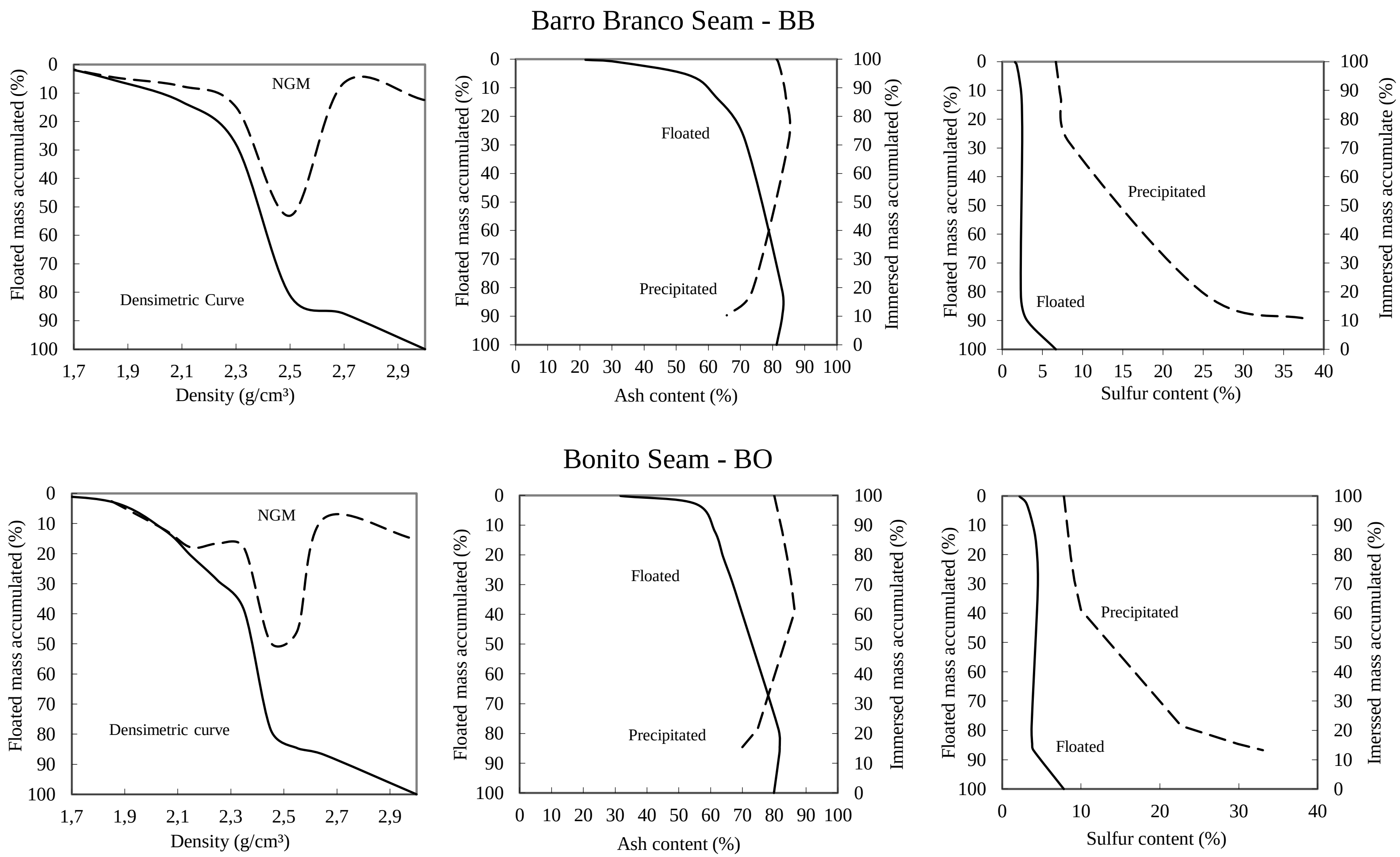

Figure 4. Washability curves of the coal waste from the BB and BO seams: near gravity material (NGM) and densimetric curve, curve of ash content, and curve of total sulfur content.

Figure 5 presents images of the material obtained for each densimetric fraction after cutting at densities 2.2 and 2.7. It is observed that in the densimetric range of less than 2.2, the material presents a darker coloration due to the presence of carbonaceous matter disseminated in the rock. The intermediate fraction, 2.2 < *d* < 2.7, has a grayish appearance, with a matte appearance due to the presence of clastic materials. The fraction with *d* > 2.7 has pyrite in the form disseminated and/or nodules.

Figure 5. Images of the energetic fraction (*d* < 2.2), intermediate fraction (2.2 < *d* < 2.7), and pyrite rich fraction (*d* > 2.7) of the Bonito seam obtained after densimetric separation.

Table 1 shows the results for the mass fraction, ash content, and sulfur forms of the raw coal tailing and the three densimetric fractions obtained after cutting at densities 2.2 and 2.7 for both seams. In relation to the mass balance, the two analyzed seams presented a similar distribution in the stipulated cutting densities. The fraction with lower density (*d* < 2.2) represents 16.2% and 20.7% of the coal waste for the BB and BO seams, respectively. Due to the amount of residual coal and lesser ash content, this fraction has potential for usage in blending with better quality coal or in co-combustion with other industrial waste that have energetic potential (Barbosa et al., 2009; Li et al., 2011; and Muthuraman et al., 2010). The material with intermediate density (2.2 < *d* < 2.7) has the highest mass ratio (68.8% for BB and 66.1% for BO), which can be considered as a low sulfur reject. Finally, the highest density (*d* > 2.7) represents 15.0% and 13.2% of the waste (seams BB and BO, respectively), with a total S content of 37.6% (seam BB) and 33.1% (seam BO). These values are considered adequate for the production of sulfuric acid (ESA/EFMA, 2000; Runkel and Sturm, 2009).

Table 1. Results of the mass fraction, ash content, and sulfur forms for each relative density obtained after cutting at densities 2.2 and 2.7 (*d* < 2.2, 2.2 < *d* < 2.7, and *d* > 2.7) and the raw coal waste of the BB and BO seams.

	Barro Branco Seam				Bonito Seam			
	Coal waste	$d < 2.2$	$2.2 < d < 2.7$	$d > 2.7$	Coal waste	$d < 2.2$	$2.2 < d < 2.7$	$d > 2.7$
Mass (%)	100	16.2	68.8	15.0	100	20.7	66.1	13.2
Ash (%)	84.2	58.5	92.7	73.1	78.6	64.0	84.2	68.8
S_{total} (%)	6.7	1.8	1.1	37.6	7.8	4.4	3.8	33.1
S_{pyrite} (%)	5.6	1.3	0.7	32.5	6.4	3.1	2.8	29.6
$S_{sulfate}$ (%)	0.2	0.2	0.1	0.4	0.2	0.2	0.1	0.6
$S_{organic}$ (%)	1.0	0.3	0.3	4.8	1.2	1.1	0.9	2.9

Although the mass proportions of each fraction are similar for the two seams, the BB seam has advantages over the BO seam due to the following aspects:

(a) lesser ash and sulfur content in the energy fraction $d < 2.2$

(b) lesser sulfur content in the intermediate fraction $2.2 < d < 2.7$;

(c) greater sulfur content in the pyrite fraction $d > 2.7$.

Thus, it is possible to perceive that the reprocessing of coal tailings in the BB seam was easier. This is due to a greater release of the material components in the BB seam than in the BO seam - carbonaceous matter, silicates, and pyrite. As can be observed in Figure 2, the BB seam is thinner but richer in coal; whereas, the BO seam is thicker, with the predominance of carbonaceous shales (Kalkreuth et al., 2010). This greater facility to separate the BB seam in relation to the BO is aware by local coal experts and has already been recorded in literature (Feil et al., 2012; Mendonça Filho et al., 2013).

Estimation of sulfuric acid production in the Santa Catarina coal region is shown in Table 2. The pyritic concentrate, regardless of the seam, is in the range of 30%-32% of pyritic S. Considering the average sulfur content of 31% (corresponding to 58.2% pyrite), an annual production of rejects of 4,135,000 tons per year (average between 1990 and 2016) and a 14% mass recovery of pyrite concentrate from the tailings, an annual production of 578,900 tons of pyrite concentrate (or 337,030 tons of pyrite) is estimated. In terms of elemental sulfur, it represents 179,750 tons per year, a 25% increase in current Brazilian production of 543,000 tons per year. This is significant considering that Brazil is dependent on imports of this raw material, with an apparent sulfur consumption of 2,750,000 tons per year (apparent consumption = production + importation – exportation), largely marketed in the form of sulfuric acid, whose main use is in the production of fertilizers (DNPM, 2016). This is equivalent, in terms of sulfuric acid, to a production of 539,245 tons per year, which currently does not exist in southern Brazil. It should be emphasized that this production could be even greater if the liabilities of the coal deposits were utilized.

Table 2. Estimation of sulfuric acid production in the Santa Catarina coal region based on the pyrites concentrate obtained in the BB and BO seams.

	Santa Catarina coal region
Average coal tailings production (tons year^{-1})	4,135,000
Estimated pyrite concentrate production (tons year^{-1})	578,900
FeS_2 content in the pyrite concentrate (%)	58.2
Estimated H_2SO_4 production (tons year^{-1})	539,245
Estimated elementary S production (tons year^{-1})	179,750

Even though pyrite concentrates can be obtained from both seams, the release difference between pyrite, inert rocks, and coal implies important environmental issues with respect to tailings generation. Table 3 presents the results of the AP, NP and NNP of the raw coal tailings samples (before densimetric separation for pyrite concentration) and intermediate fraction after removal of the pyritic fraction) for the BB and BO seams.

Table 3. Acidity potential (AP), neutralization potential (NP), and net neutralization potential (NNP) of the raw coal waste and intermediate fractions (2.2 < *d* < 2.7) of the Barro Branco and Bonito seams.

	Barro Branco Seam		Bonito Seam	
	Coal waste	2.2 < *d* < 2.7	Coal waste	2.2 < *d* < 2.7
AP (kg $CaCO_3$ t^{-1})	209.4	34.4	244.0	119.4
NP (kg $CaCO_3$ t^{-1})	0.0	0.0	24.1	39.1
NNP (kg $CaCO_3$ t^{-1})	-209.4	-34.4	-219.8	-80.3

The coal tailing of the BB deposit has a lower acidity potential than the BO seam. In addition, considering the mass ratio and AP of the intermediate fraction, the BB seam reduced the acidity by 90% compared to the raw reject and BO reduced it by only 65%. The NP, due to the presence of carbonates in the rock, was zero for the BB seam and 24.1 kg $CaCO_3$ ton^{-1} for the BO seam. As the neutralization values were considerably lower than those of acidification, the NNP was negative for both rejects. The intermediate fraction of the BB seam had an NNP of -34.4 kg $CaCO_3$ ton^{-1} and the BO seam of -80.3 kg $CaCO_3$ ton^{-1}, indicating a higher net acidity potential for the latter. When high values of acidity occur, assuming that this material is disposed in waste deposits, the risks of contamination to the environment increase, as well as the costs of the treatment plants because of the need for a greater amount of neutralizing agents to treat ARD (Weiler et al., 2016).

Thus, the gravimetric concentration of the pyrite present in the mineral coal tailings of the Santa Catarina coal region makes it possible to concentrate the pyrite and reduce the acidity generation potential of the tailings generated during the mineral processing. The production of sulfuric acid is important in the economic context of Brazil, as the country consumes large quantities for the production of fertilizers used in agriculture (Vale, 2017). It should be noted that, in the past, the company Carboquímica Catarinense (ICC), has already conducted this process, when there was a planning for pyrite's use in the region (1970-1990). However, its activities were closed for political and economic reasons (Souza, 2007). There is an important amount of sulfur associated with Brazilian coal (DNPM, 2016) and the country fails with the breakdown of the production chain, already established in the past, not making full use of its resources. In the present day, when we talk about the substitution of linear economy for the circular economy (Blomsma and Brennan, 2017; Lèbre et al., 2017), the fact is even more evident.

Even more, noteworthy are the growing exploration of the BO seam in recent years and the production decline of the BB seam (Figure 6). In the year 2000, approximately 70% of the coal production in the region was from the BB seam and 30% from the BO seam. Currently, the scenario has reversed, so that the BB seam contributes to approximately 35% of the production and the BO seam to 65%.

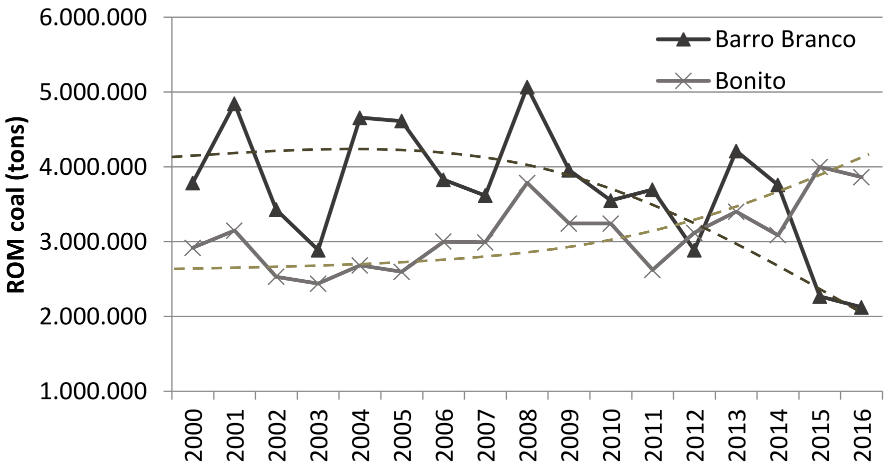

Figure 6. Comparison of the run-of-mine (ROM) coal exploitation increase of the Bonito seam and decline of its exploitation in the Barro Branco seam in the Santa Catarina coal region. Dashed lines indicate the data trend.

This change also opens challenges related to the knowledge, management, and destination of the products of the mining of the BO seam, demanding research and development actions that contribute to the regional (environmental aspects) and national scenario (minor importation of sulfur). Among the main challenges are the suitability of the coal beneficiation plants for pyrite concentration and the environmentally correct management storage, transport, and destination of the material, avoiding for example the generation of acidic waters and spontaneous pyritic combustion events. The effective implementation should overcome viability barriers, necessarily through technological, managerial, structural, and cultural changes of all stakeholders - society, companies, and public authorities.

Conclusion

The coal tailings from the Barro Branco seam and the Bonito seam can be processed by gravimetric processes to obtain concentrates with 30%-32% pyritic sulfur. When comparing the remaining coal tailings, after removal of the pyrite, it is possible to observe a considerable reduction of the acidity generation potential. Owing to the greater difficulty in the concentration of pyrite, the intermediate fraction of the Bonito seam presents a higher sulfur content and a higher potential for acidity generation. Nevertheless, this study showed that the use of pyrite from coal tailings could bring economic and environmental benefits if appropriate procedures are followed. From planning for the use of pyrite in the Santa Catarina coal region, the tailings could be used to produce sulfuric acid, contributing to the Brazilian supply of this input and reducing the environmental impacts caused by rejects disposal.

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4. THE USE OF STATIC AND HUMIDITY CELL TESTS TO ASSESS THE EFFECTIVENESS OF COAL WASTE DESULFURIZATION ON ACID ROCK DRAINAGE RISK.

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The use of static and humidity cell tests to assess the effectiveness of coal waste desulfurization on acid rock drainage risk

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ABSTRACT

The environmental benefits of waste desulfurization were evaluated in the Santa Catarina coal field, Brazil. Coal waste from a beneficiation plant was separated into three density fractions, using a two stage process. Characterization of these fractions indicated that the low ($D < 2.2$ g cm^{-3}) and high ($D > 2.7$ g cm^{-3}) density fractions were potentially suitable for energy and sulfuric acid production, respectively. The waste fraction of intermediate density ($2.2 < D < 2.7$ g cm^{-3}) represented 69% of the total mass studied and had a relatively low sulfide content, and it was postulated that it may be suitable for land disposal with minimum risk to the surrounding environment. This hypothesis was tested using laboratory-scale static and kinetic tests, which indicated that although the fraction remained net acid generating, the rate and net amount of metals, salts, and acidity that leached was considerably less than that of the discards before separation. It was concluded that this approach could reduce the amount of waste generated, as well as the associated pollution risk.

Keywords: Zero waste, Acid mine drainage, Two-stage separation, ARD prediction tests

Introduction

Coal mining and beneficiation operations generate a considerable amount of industrial solid waste in terms of production, accumulation volume, occupied area, and acid rock drainage (ARD) generation (Bell et al. 2001; Bian et al. 2010; Komnitsas et al. 2001; Simate and Ndlovu 2014). The ARD can contaminate regional surface and groundwater or the land, with toxicity levels depending on discharge volume, pH, total acidity, concentration of dissolved metals, and buffering capacity of the receiving streams (Akcil and Koldas 2006; Kontopoulos 1998).

Approximately 6.5 million tonnes (t) a year of coal waste were generated in Brazil during the years 2008–2014, almost 80% of which was in the state of Santa Catarina (SIECESC 2014). The grade of coal deposits in Brazil is relatively low, and approximately 65% of the run-of-mine (ROM) coal extracted from underground mines in the carboniferous region of Santa Catarina is discarded in waste dump deposits. In addition, inadequate waste management in the past has left a devastating legacy in this region, with pollution plumes extending more than 6000 ha over several catchment areas. Local studies have indicated considerable contamination of the Araranguá, Tubarão and Urussanga river basins, with reduced pH and high concentrations of metals and sulfate (Gomes et al. 2011; SIECESC 2014).

Currently, Brazilian coal mining operations emphasize an end-of-pipe treatment approach to coal waste and ARD management (Silva and Rubio 2009; Silveira et al. 2009). Chemical ARD treatment techniques such as lime neutralization typically consume large amounts of expensive reagents, generate significant quantities of sludge, and are only effective in reducing ARD risks in the short term. As pointed out by Kontopoulos (1998), many of these shortcomings can be overcome by implementing preventative techniques that minimize the generation and the subsequent dispersion of ARD from waste dump deposits. One such approach entails the pre-disposal removal of ARD generating sulfide minerals by means of physical separation techniques such as flotation and density separation. Apart from reducing ARD risk, integration of a sulfide removal step into the beneficiation circuit also offers opportunity for additional value recovery (Amaral Filho et al. 2013; Benzaazoua et al. 2008; Hesketh et al. 2010; Hilson 2000; Kazadi Mbamba et al. 2012).

The ability to accurately predict the ARD-generating potential of wastes plays an important and essential role in the development of effective approaches and technologies for mitigating associated impacts and liabilities. Methods for quantifying the ARD potential of sulfide wastes can be classified as either static or kinetic tests. Static testing methods are short term (hours to days) tests that ignore the relative rates of acid-forming and neutralizing reactions, while kinetic testing methods are long term (months to years) tests that allow for the study of the dynamic factors influencing ARD generation (Barbosa et al.

2009; Lapakko and Antonson 2006; Lengke et al. 2010; Sapsford et al. 2009, US EPA 1994). Although a number of kinetic test protocols have been developed and some adaptations and protocol improvements suggested—for example, to simulate conditions of waste rock piles in an arid environment (Lapakko and Trujillo 2015) or to avoid excessive drying of the sample (Bouzahzah et al. 2015)—humidity cell tests follow a standard procedure and are recommended for ARD prediction (ASTM 2007a).

The objective of this study was to evaluate the environmental implications of desulfurizing coal waste by dense medium separation. The separated fractions were characterized and the rate and extent of release of acid and metals from the bulk discards (separation feed) and separated sulfide-lean tailings fraction were determined using laboratory-scale static and humidity cell tests.

Methods

The coal waste was collected in the state of Santa Catarina from the Verdinho Mine preparation plant, which extracts the Barro Branco seam. Specifically, the sample was collected from the discards of the coarse (average diameter between 2 and 50 mm) particle processing (jigging) circuit, which is responsible for 85% of the total waste rock production.

About 90% of the total sulfur is removed as part of this fraction during the coal beneficiation process. The material (bulk discards) was subjected to laboratory-scale dense medium (Fe–Si) separation tests to attain three density fractions (D): a low density ($D < 2.2$ g/cm3) coal-rich fraction; an intermediate density ($2.2 < D < 2.7$ g cm^{-3}) sulfide-lean fraction; and a high density ($D > 2.7$ g cm^{-3}) sulfide-rich fraction. Atomized ferrosilicon was mixed with water to obtain suspensions of 2.2 and 2.7 g cm^{-3}. Suspension densities were measured by a densimeter. All three density fractions (products) were weighed and subjected to standard proximate (ASTM 2007b), ultimate (ASTM 2009), and chemical speciation (ASTM 2002) analysis.

Static and kinetic ARD prediction tests were carried out on the bulk (pre-intervention) discards and low-sulfide intermediate density fraction ($2.2 < D < 2.7$ g cm^{-3}) samples to evaluate and compare their acid-generating potentials before and after coal and pyrite recovery.

Static ABA methods are widely used as a screening procedure. In this study, the static tests were performed by both acid-base accounting (ABA) and modified acid-base accounting (MABA) (Sobek et al. 1978, US EPA 1994) to determine the balance between acid production and consumption (neutralization) by the mineral components of the samples. The particle size of the samples was reduced to less than 0.25 mm. Acidity potential (AP) was determined by total sulfur analysis for ABA and sulfide sulfur for MABA. Total sulfur was measured using a Leco Analyzer and sulfide sulfur by ASTM D 2492 (ASTM 2002).

The bulk discard and intermediate density fraction samples were also subjected to long-term humidity cell tests, in accordance with the ASTM D 5744 procedure, “Standard test method for accelerated weathering of solid materials using a modified humidity cell” (ASTM 2007a). This procedure was carried out for 92 weeks (21 months) and the leachates were analyzed for the following parameters: pH, redox potential (Eh), acidity, and concentrations of sulfate and metals (Al, Mn, Zn, and Fe). Analyses were conducted weekly, following the procedures of the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). The procedure was carried out without bacteria inoculation; however, the presence of *Acidithiobacillus ferrooxidans* in the leachates was monitored, and reached 105 MPN:100 mL after the 15th week. Based on the kinetic test results, the pyrite oxidation rates were calculated in terms of kg of pyrite per ton of coal waste per day (kg t^{-1} day^{-1}). Weekly average temperatures were obtained from a local weather station to assess the potential influence of temperature on the experimental results.

Results and Discussion

Density separation

Results of the density separation tests indicate that 17% of the coal discards has a density lower than 2.2 g cm^{-3}, 69% a density of between 2.2 and 2.7 g cm^{-3}, and 14% a density higher than 2.7 g cm^{-3}. The characterization results for the bulk discards and discard fractions after density separation are shown in Table 4.

Table 4. Characteristics of the downstream discards samples preintervention and after density separation by ferrosilicon medium dense.

	Bulk Discards	Low density fraction[1]	Intermediate density fraction[2]	High density fraction[3]
a) Proximate analysis (%)				
Ash	84.2	77.4	90.4	65.3
Volatile Matter	12.3	11.8	8.6	27.8
Fixed Carbon	3.5	10.7	1.0	6.9
b) Ultimate analysis (%)				
C	6.7	16.4	3.9	8.9
H	1.2	1.8	1.1	0.9
N	0.3	0.5	0.3	0.3
S	7.0	1.8	1.1	37.7
c) Forms of sulfur (%)				
Pyritic sulfur	6.0	1.3	0.7	32.5
Sulfate sulfur	0.1	0.2	0.1	0.4
Organic sulfur	0.9	0.3	0.3	4.8

1.D<2.2 g cm^{-3}; 2. 2.2<D<2.7 g cm^{-3}; 3. D>2.7 g cm^{-3}

While all samples had a relatively high total ash content, the low density fraction (<2.2 g cm^{-3}) was enriched in carbonaceous matter (16.4% carbon) and depleted in sulfur (1.8% total sulfur). Previous studies (Li et al. 2006, 2011; Muthuraman et al. 2010) have demonstrated the feasibility of co-combusting high ash coal with carbonaceous wastes to produce energy. Most (≈80%) of the pyritic sulfur in the feed is reported to the high density fraction. This fraction had a pyritic sulfur content of 32.5%, equivalent to 61% pyrite. Pyrite roasting has been used worldwide to produce sulfuric acid (Runkel and Sturm 2009). Although comprising the bulk of the discard material (69% by mass), the pyritic sulfur content in the fraction of intermediate density (2.2 < D < 2.7 g cm^{-3}) was relatively low (0.7%), amounting to less than 10% of the pyritic sulfur in the feed discards.

Static ARD tests

The results of the subsequent static ARD tests, conducted on the bulk discards (before density separation) and the intermediate density fraction (2.2 < D < 2.7 g cm^{-3}), are summarized in Table 5. Both samples were classified as acid forming by both the traditional (ABA) and modified (MABA) test results. This can be attributed to the negligible neutralizing capacity (NP = 0) of both samples. Nevertheless, a comparison of the static test results indicates that the fraction of intermediate density has a significantly lower acid production

(AP) potential and higher net neutralizing potential (NNP) than the bulk discards, due to the reduced pyritic sulfur content.

Table 5. - Static ARD prediction tests for the bulk coal discards and intermediate density fraction samples

	AP (kg $CaCO_3$/t)		NP (kg $CaCO_3$/t)		NNP (kg $CaCO_3$/t)	
	ABA	**MABA**	**ABA**	**MABA**	**ABA**	**MABA**
Bulk discards	217.3	196.9	0.0	0.0	-217.3	-196.9
Intermediate density fraction	35.0	22.5	0.0	0.0	-35.0	-22.5

Humidity cell tests

The time-related profiles for the humidity cell tests conducted on the bulk discard and intermediate density fraction samples are summarized in Figure 7. Both samples generated slightly acidic leachates from the beginning of the tests, with pH values in the region of 4.5. These pH values continued to decline steadily, stabilizing at approximately 2.0–2.5 after 30 weeks. The bulk discard sample presented slightly lower pH values than the intermediate density fraction sample throughout the experiment. It is also possible to observe that the pH of the leachate of the intermediate fraction increased slowly after a period of 80 weeks. Redox potentials increased from initially low values of around 300 mV to peak values between 550 and 600 mV after 13 and 22 weeks for the bulk discard and intermediate density fraction samples, respectively. Redox potentials >550–600 mV at pH values <3 are generally indicative of rapid oxidation of ferrous iron and sulfide minerals, and are normally associated with microbial activity (Acharya et al. 2001; Hesketh et al. 2010; Kazadi Mbamba et al. 2012).

The significant increases in the soluble iron, sulfate, and acidity after 13 and 22 weeks for the bulk discard and intermediate fractions, respectively, are consistent with the onset of rapid and extensive pyrite oxidation at these time intervals. Similar leach profiles were obtained for other metals, with the onset of rapid pyrite oxidation being accompanied by a significant increase in the soluble concentrations of Al, Zn, and Mn. A comparison of the humidity cell leach profiles for the bulk discards and intermediate density fractions indicates that the pyrite oxidation and release of acidity occurs at a faster rate and to a significantly greater extent in the case of the bulk discard sample (Figure 8).

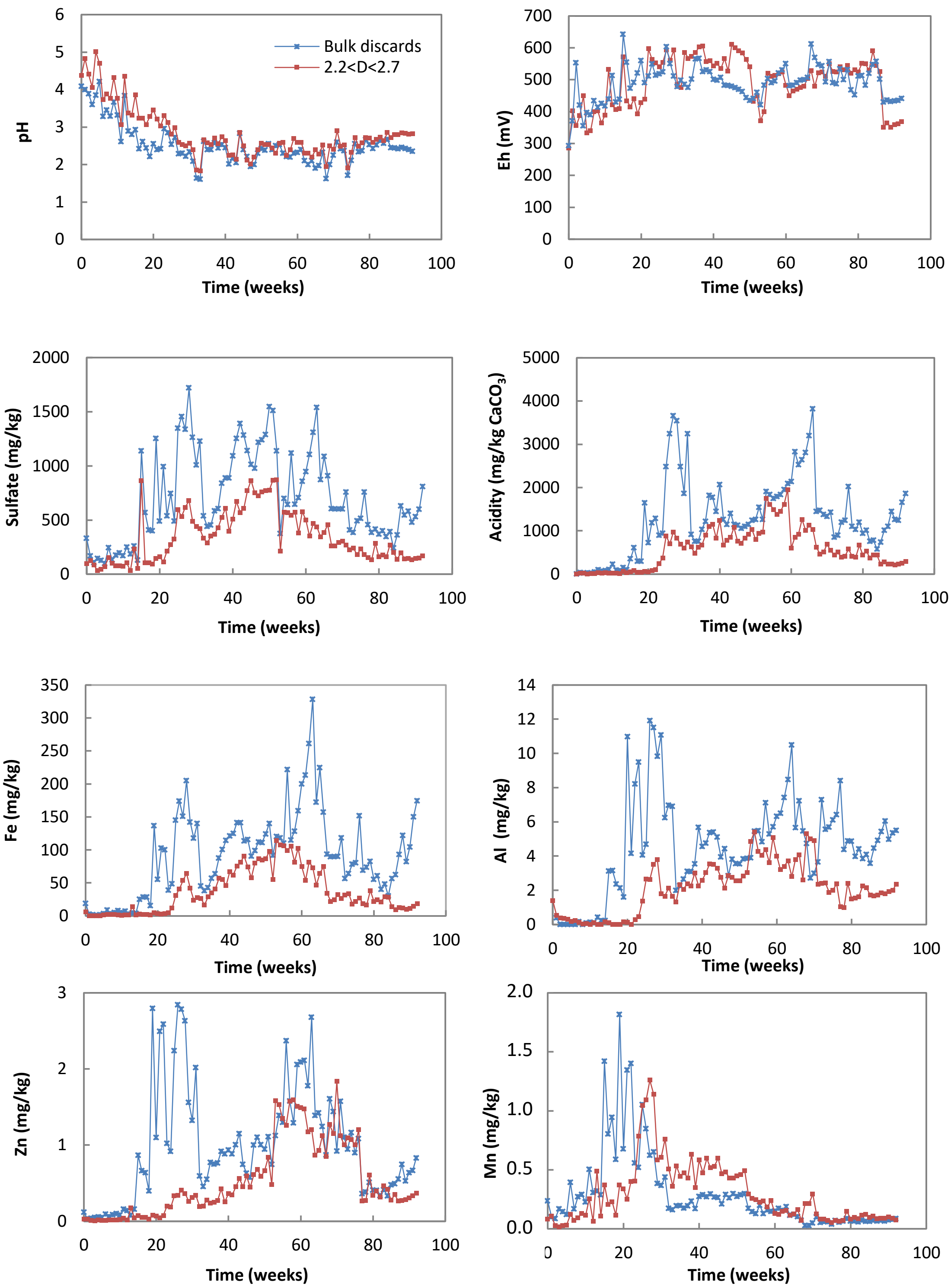

Figure 7. Plot of humidity cells test profiles for the bulk discard and sulfide-lean intermediate density fraction (2.2–2.7 g cm^{-3}) samples.

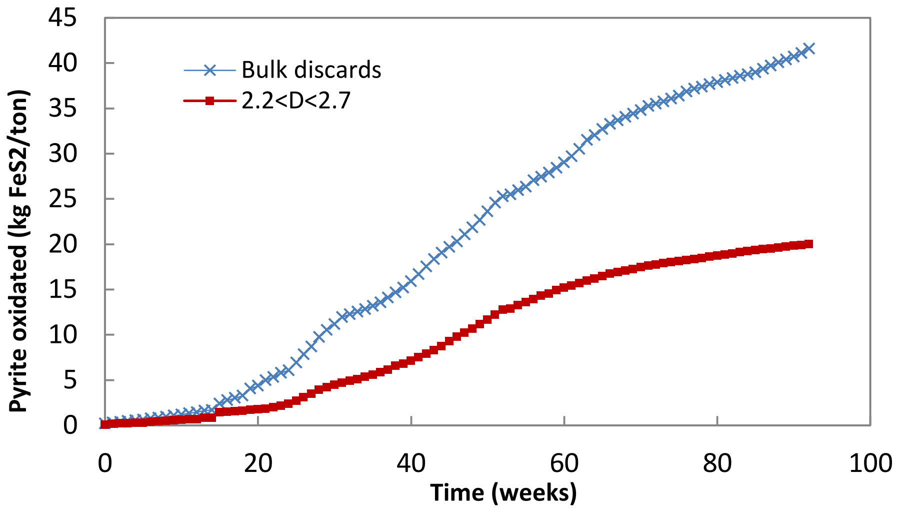

Figure 8. Plot of accumulated pyrite oxidation profiles for the bulk discard and sulfide-lean intermediate density fraction (2.2–2.7 g cm^{-3}) in 92 weeks time.

A comparison of the accumulated release values over the 92 week leach period (Table 6) confirms that, with the exception of Mn, density separation decreased soluble metal concentrations by up to 60%, and decreased the release of sulfate ions by 51% and acidity by 55%.

In the case of the bulk discards, at 92 weeks, 8595 mg kg^{-1} of cumulative Fe was leached whilst cumulative releases of Mn, Zn, and Al were 27, 92, and 424 mg kg^{-1}, respectively. In contrast, the cumulative amount of Fe leached from the intermediate density fraction, obtained from processing the bulk discard, amounted to 3434 mg kg^{-1} after the same time, with cumulative releases of Mn, Zn, and Al of 27, 48, and 196 mg kg^{-1}, respectively.

Table 6. Comparison of the accumulated release values over the 92 week leach period.

	Bulk discards	Intermediate density fraction	Difference (%)
Fe (mg kg^{-1})	8595	3434	60
Al (mg kg^{-1})	424	196	54
Zn (mg kg^{-1})	92	48	48
Mn (mg kg^{-1})	27	27	0
Acidity (mg $kgCaCO_3^{-1}$)	120568	53682	55
Sulfate (mg kg^{-1})	65746	32289	51

Based on sulfate release, calculated pyrite oxidation rates averaged 64 and 32 g FeS2 t^{-1} day^{-1} for the bulk discards and desulfurized tailings fraction, respectively. However, the pyrite oxidation rate of the bulk discards remained approximately constant while it started to decrease for the intermediate density fraction over the second half of the experiment. Sulfur balances furthermore indicated that 98% of the S present in the desulfurized coal waste fraction was consumed in the 92 week period compared to only 31% of the S in the bulk discards. This is indicative of incomplete oxidation of the pyrite and release of acidity, salts, and metals from both samples, but more so from the bulk discards. Longer leach periods are thus likely to produce significantly higher total cumulative release values for the bulk discard sample relative to the desulfurized fraction.

The molar Fe:S ratio in the leach liquors was consistently less than the stoichiometric ratio of 0.5 for pyrite (Figure 9). This is attributed to the high solubility of sulfate relative to that of ferric iron Fe^{3+}, which is partially adsorbed onto coal waste particles or precipitated as hydroxides/oxyhydroxides. The precipitation/adsorption of iron is pH dependent and favored at pH values greater than 3.0, which occurred during the first weeks in both humidity cells and, in the case of the desulfurized fraction, after week 80. Similar trends were observed by Sapsford et al. (2009) during humidity cell leaching of a metalliferous (Cu–Zn–Pb) mine waste.

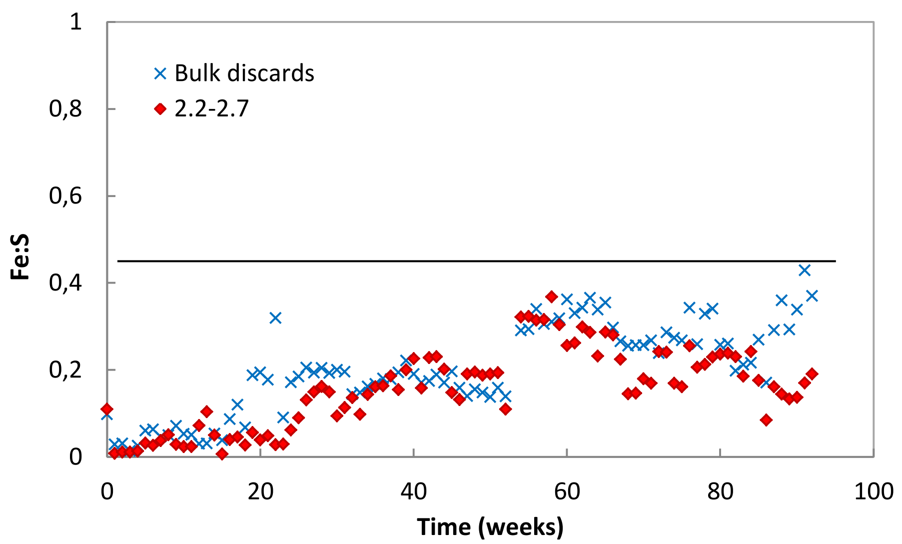

Figure 9. Molar ratio Fe:S in the humidity cell leachates

Figure 10 compares the release rate of acidity for the bulk discards sample with temperature fluctuations. With the exception of an initial lag period for the first 20 weeks, the graph shows a trend of increasing acidity release from the bulk discards in the hottest period (summer). This trend can probably be attributed to increased activity of *A. ferrooxidans* bacteria, whose optimum growth temperature is 30 °C (Johnson and Hallberg 2005; Lundgren et al. 1972), in the warmer months. The lag period may be due to the time required for establishment of the microbial population and acclimatization.

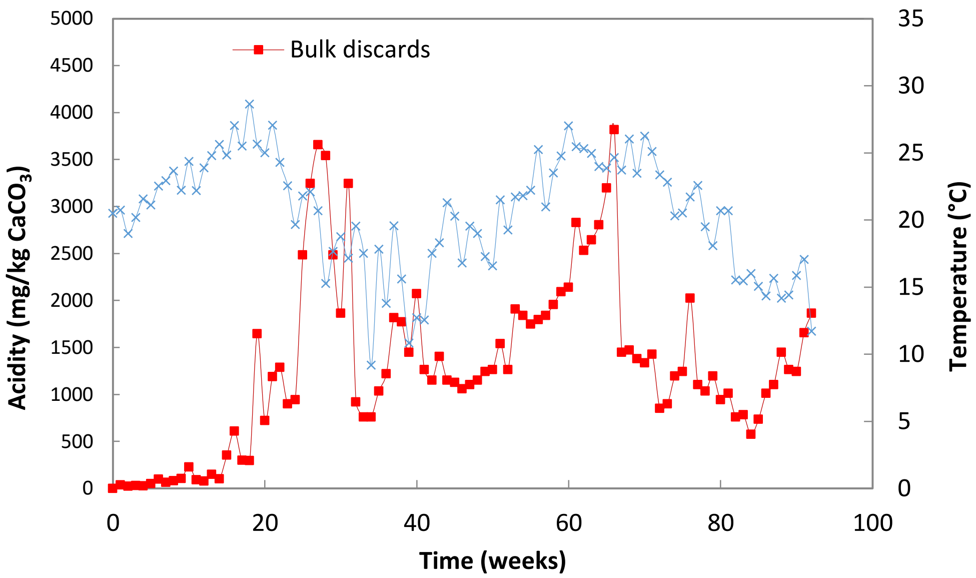

Figure 10. Acidity release profiles and temperature fluctuations for the humidity cell tests on the bulk discards (before intervention).

Conceptual Approach

Traditionally, ARD generated by coal waste piles is treated using conventional techniques such as lime neutralization. This represent a long-term cost to the coal producers, who are coming under increased pressure (by public and government spheres) to adopt more preventive approaches in line with cleaner production and sustainable development principles. In the approach proposed here, bulk discards are separated into three density fractions, a coal-rich low density fraction, a sulfide-rich high density fraction, and an intermediate density fraction with a reduced sulfide content. It is further proposed that the coal-rich and sulfide-rich fractions have the potential to be used and integrated back into the local economy through their use as feedstock for energy production, by combustion or gasification, and sulfuric acid production, by roasting, respectively. Apart from improving resource efficiency and providing opportunities for coal mines to enhance their profitability through product diversification, the proposed approach also has a number of environmental benefits. These include a reduction in the net volume of waste requiring disposal and a leachate containing less salts and toxic components. Although leachate treatment is still likely to be required to meet acceptable water quality standards, the reduced acidity and salt loads will lower capital and operating costs, and reduce the amount and hazardous properties of the sludge generated by conventional ARD treatment. Despite the obvious economic and environmental benefits, the successful implementation of such an approach will require effective engagement and collaboration between all potential stakeholders (Fan et al. 2014; Haibin and Zhenling 2010; Hilson 2003; Reddick et al. 2008; McLellan et al. 2009).

Conclusion

The results of this test work show that pre-separation of coal waste discards into different density fractions reduces the amount and hazard of the disposable waste. The waste fraction of intermediate density, which contained less sulfur, represented 69% of the total mass studied. Static and humidity cell tests were used to assess the effect of coal waste desulfurization on ARD risk. They indicate that this separated waste fraction had significantly less ARD-generating potential than the bulk discard sample, resulting in reduced release of metals, salts, and acidity into solution over the long-term. Reprocessing coal waste thus has the potential to both reduce the economic and environmental burdens associated with coal waste, and improve the net material efficiency of the coal sector.

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5. COAL WASTE DERIVED SOIL-LIKE SUBSTRATE: AN OPPORTUNITY FOR COAL WASTE IN A SUSTAINABLE MINERAL SCENARIO.

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Coal waste derived soil-like substrate: an opportunity for coal waste in a sustainable mineral scenario.

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Abstract

Proper coal waste management significantly reduces environmental impacts. An option to address this issue is to reduce coal waste accumulation by transforming it into soil. The objectives of this study were to process coal waste by turning it into a soil-like substrate - SLS (a kind of spolic technosol) and to evaluate plant growth and possible changes in sulfur speciation. Coal waste was desulfurized by gravity processing, ground, and amended with rice husk ash, steel slag, and sewage sludge to improve physical structure, adjust acidity, and provide organic matter as well as nutrients. *Megathyrsus maximus var. maximus* (Guinea grass) was cultivated in a SLS for 100 days (whole cycle). Results demonstrated healthy growth of Guinea grass. Plant growth, total sulfur and sulfur species (S-sulfate, S-pyrite, S-organic) were analyzed. Data indicated that soil mixtures underwent a 50% reduction of S-pyrite, an increase of S-organic and had high fertility measurements. The study showed promising results for the use of coal waste as a soil-like substrate to improve mining sustainability.

Keywords: mining, technosols, environmental management, sustainability

Introduction

Coal plays a vital role in providing electricity, steel, cement and coal-to-liquid fuels worldwide. However, mining, ore beneficiation and ore use are associated with a number of environmental impacts. Coal mining’s major problems are waste generation (Bian et al., 2009); subsidence (Bell et al., 2001); acid rock drainage (ARD); pollution of soils, water, and air (Komnitsas et al., 2001); greenhouse gas emissions (Bi et al., 2017; Guo et al., 2017;

Burmistrz et al., 2016); and related socio-environmental problems (Ruiz et al., 2014). Therefore, initiatives to minimize environmental impacts are important for improving sustainability in all coal production cycle (Wang, et al., 2017; Krzemień et al., 2016; Anawar, 2015; Franks et al., 2011; Si et al., 2010; Bian et al., 2010).

Many coal deposits are associated with sulfur which can be present as S-FeS_2 (pyrite), S-SO_4 (sulfate), and S-organic. Pyrite, in the presence of water, oxygen, and acidophilic bacteria, oxidizes and, if lacking neutralizing minerals such as carbonates, generates acid rock drainage. Acid drainage can cause extensive contamination of regional surface water, groundwater and soil, with toxicity levels dependent on discharged volumes, pH, total acidity, concentration of dissolved metals, and buffering capacity of the receiving streams (Akcil and Koldas, 2006; Kontopoulos, 1998; Simate and Ndlovu, 2014).

The Brazilian coal mining region in the state of Santa Catarina feeds the Jorge Lacerda Thermoelectric Plant Complex, the largest thermoelectric power plant in South America, with an installed capacity of 852 MW (Kalkreuth et al., 2016). The grade of the coal deposits is relatively low and the coal is strongly associated with silicates and pyrite (Kalkreuth et al., 2010). After concentration procedures, approximately 65% of the run-of-mine (ROM) coal extracted from underground mines is discarded in waste deposits. On average, sulfur content in this coal waste is about 6%, most of it in the pyritic form (S-FeS_2), corresponding to 12% pyrite by mass. In addition, inadequate waste management in the past has left a devastating legacy in this region. It is estimated that in the state of Santa Catarina there are more than 300 million tons of coal waste with pollution plumes extending over more than 6,000 ha. Also about 800 km of the Araranguá, Tubarão and Urussanga river basins have been left with lowered pH and high concentrations of metals and sulfate (Gomes et al., 2011; SIECESC, 2014).

Considering the environmental problems associated with inappropriate coal waste management, there have been some attempts to reprocess and desulfurize coal waste to minimize ARD formation (do Amaral Filho et al., 2017) and to find other applications such as backfilling, soil fabrication, afforestation, and use as construction material (Bian et al., 2009; dos Santos et al., 2013; García Giménez et al., 2016; Haibin and Zhenling, 2010; Taha et al., 2016).

Desulfurized coal waste was suggested by Firpo et al. (2014) to be used as the main material for a coal derived soil-like substrate (a kind of technosol) after being amended with organic matter, an alkalinity source, and a physical structure conditioner. Technosols, according to FAO soil classification, are artificial soils derived from the mixture of anthropic materials whose properties and pedogenesis are dominated by their technical origin; they include soils from wastes like landfills, sludge, cinders, mine spoils and ashes (IUSS Working Group WRB, 2014). Technosols are often referred to as urban or mine soils; the mine soils' chemical, physical, and biological properties depend greatly upon the rock and soil mixes, soil amendments, geomorphology, hydrology, and vegetation introduced (Wick, 2010).

The objective of this study was to process coal waste with amendments to turn it into a coal derived soil-like substrate (SLS). Plant growth and possible changes in sulfur speciation were also evaluated. The study was carried out in plant containers with the graminoid *Megathyrsus maximus var. maximus* (Guinea grass) irrigated with rainwater to field capacity.

Material and Methods

Four materials were selected: coal mine waste (as a primary constituent), steel slag (alkalinity and micronutrient source), sewage sludge (nutrient and organic matter supply), and rice husk ash (physical structure).

Coal waste was obtained directly from a coal preparation plant that mines the Barro Branco seam (state of Santa Catarina, Brazil). Specifically, the sample was collected from the discards of the coarse (average diameter between 2 and 50 mm) particle processing (jigging) circuit, which is responsible for 85% of the total waste rock production.

The material (bulk discards) was subjected to laboratory-scale dense medium separation to attain three density fractions: i) a carbonaceous-rich fraction with a density lower than 2.2 g cm^{-3} ($CW_{<2.2}$), ii) a sulfide-rich fraction with a density higher than 2.6 g cm^{-3} ($CW_{>2.6}$), and iii) a coal and sulfide lean intermediate fraction with a density between 2.2 and 2.6 g cm^{-3} ($CW_{2.2\text{-}2.6}$). The separation was achieved by mixing the dense organic liquids tribromomethane ($CHBr_3$) and tetrachlorethylene (C_2Cl_4) to obtain liquids with densities of 2.2 and 2.6 g cm^{-3}. Liquid densities were prepared with the aid of a densimeter. All three density fractions (products) were weighed and analyzed for moisture, volatile matter, fixed carbon and ashes - standard proximate analysis (ASTM, 2007); carbon, hydrogen, nitrogen and sulfur (CHNS) elemental composition - ultimate analysis (ASTM, 2009); and pyritic, sulfuric and organic sulfur speciation (ASTM, 2002). Fractions were also subjected to X-ray diffraction (analysis of crystalline compounds).

Steel slag samples were obtained from a secondary refining furnace in a carbon steel plant. Sewage sludge samples came from an upflow anaerobic sludge blanket (UASB) reactor operating in a local sewage water treatment plant. Rice husk ash was obtained from a rice processing plant. All samples were collected according to Brazilian sampling standards (ABNT, 2004). The intermediate coal waste density ($CW_{2.2\text{-}2.6}$) and steel slag were ground in a jaw crusher followed by a roller mill crusher to a particle size below 2 mm. Sewage sludge was dried at 60º C and pounded to break up the clods. An Elementar Vario Macro analyzer was used to obtain the percent elemental compositions of $CW_{2.2\text{-}2.6}$, steel slag, sewage sludge, and rice husk ash for carbon, hydrogen, nitrogen and sulfur (Table 7).

In order to determine the ratio of coal mine waste to steel slag capable of producing a circumneutral soil pH, net neutralization potential (NNP) was obtained following the modified Acid Base Account (ABA) method (Lawrence and Scheske, 1997). Modified ABA is a static test procedure that determines acid potential (AP) generation based on pyritic content (S-FeS_2). S-pyritic, multiplied by 31.25, equals AP in kg of $CaCO_3$ per metric ton. Neutralization potential (NP) was obtained after leaching the sample with HCl, at room temperature for 24 h, followed by titration with NaOH until a pH of 8.3 was obtained. Net neutralization potential (NNP) corresponds to the difference between NP and AP and is used to estimate acid generation. NNP values around zero indicate neutrality. Negative values denote the potential for acid drainage formation while positive values indicate that acid generation is not likely, and extra alkalinity will be present. No NP was found in $CW_{2.2\text{-}2.6}$, nor AP in steel slag. Neutrality, in the present system, was attained with a mixture of 19 parts of coal $waste_{2.2\text{-}2.6}$ to one part steel slag (Table 7).

Table 7. CHNS elemental composition of materials, acid base accounting and coal waste and steel slag ratio for neutrality.

	$CW_{2.2\text{-}2.6}$	Steel slag	Sewage sludge	Rice husk ash
Elemental analysis (%)				
C	4.15	1.03	21.5	1.33
H	1.16	0.16	5.20	0.25
N	0.18	0.82	2.70	0.92
S	0.80	0.19	8.40	0.20
Acid-base accounting test (kg $CaCO_3$ t^{-1})				
AP	25.0	0.0	-	-
NP	0.0	488.1	-	-
NNP	-25.0	488.1	-	-
Coal $waste_{2.2\text{-}2.6}$ and steel slag ratio				
	19:1			

AP – acid potential

NP – neutralization potential

NNP – net neutralization potential = (PN - PA)

Three plant containers (herein "containers") were filled with a soil-like substrate (SLS) prepared as shown in Table 8. Steel slag was added to achieve a circumneutral soil pH; rice husk ash was chosen to improve soil physical structure and avoid compaction, while sewage sludge was used to attain a final mixture with 2% organic matter.

Table 8. Soil-like substrate (SLS) composition.

Waste Material	Mass (g)	Criteria
Coal $waste_{2.2\text{-}2.6}$	887.7	main substrate
Steel slag	46.7	Modified acid-base accounting (Lawrence and Scheske, 1997)
Sewage sludge	47.8	2% organic matter w/w, (CQFS - Núcleo Regional Sul, 2004)
Rice husk ash	17.8	2% w/w, (Islabão, 2013)

The containers (930 cm^3 PVC with a screened bottom) were filled with 1 kg of SLS. Each container was seeded with *M. maximus* (Jacq.) var. *maximus* (five seeds per container) and kept on a bench exposed to sun and rain. Soil water field capacity (WFC) was measured using a tension table (Cameron and Buchan, 2006; Cooper, 2016) and, whenever necessary, irrigation was carried out with stored rain water whose composition is shown in Table 9. As routinely practiced in soil assays, soil's moisture content was kept between 50 and 60% of WFC to maintain mineralization and microbial activity at a proper and stable rate (Carter and Gregorich, 2008; Rey et al., 2005; Parfitt et al., 2005). Data obtained and released by the city of Porto Alegre (CEIC, 2016) indicated 445 mm of rainfall equivalent during the experiment.

Table 9. Rainwater composition used for irrigation.

Parameters	Rainwater (mg L^{-1})
pH	5.0
Cl^-	< 0.5
NO_3^-	< 0.2
SO_4^{2-}	6.4
Ca^{2+}	7.8
Mg^{2+}	0.8
K^+	< 0.6
Na^+	3.7

After 100 days, close to the end of the *M. maximus* life cycle, above ground plant tissue was cut, dried at 60 °C in a constant flux oven and weighed. In order to determine underground plant tissue mass, the containers were opened and the roots were carefully separated from the SLS, washed with distilled water, dried at 60 °C, and weighed. Both above and underground plant tissues were ground to pass a 60# (0.25 mm) sieve and analyzed for total sulfur content using an LECO S-144 DR sulfur analyzer.

Three SLS samples from each container were gathered before and after plant growth (18 samples total). All samples were ground to pass a 60# sieve to determine total sulfur and its speciation (S-pyritic, S-sulfate, S-organic). Total sulfur was measured in a LECO analyzer while sulfur speciation followed ASTM protocol (ASTM, 2002). Organic sulfur was considered to be total sulfur minus S-sulfate and S-pyritic.

Finally, in order to understand the potential use of SLS for plant growth, samples were analyzed in terms of net neutralization potential (NNP) and fertility. Net neutralization potential (NNP) was obtained by modified ABA (Lawrence and Scheske, 1997). Fertility parameters and methods were: clay content (clay densimetric method); pH (pH_{H2O} 1:1); lime requirement (Shoemaker-McLean-Pratt - SMP buffer method); P and K (Mehlich 1); organic matter (humid digestion), exchangeable Ca, Mg, Al and cation exchange capacity - CEC (KCl 1 mol L^{-1} extraction); Cu, Zn, and Mn (HCl 0,1 mol L^{-1} extraction); S-SO_4 ($CaHPO_4$ 500 mg L^{-1} of P); B (hot water extraction).

The experiment was run in Porto Alegre, Brazil (30°01'42"S / 51°13'42"W; Cfa Köppen-Geiger climate), during the summer. *M. maximus* is native to Africa and was chosen for being resistant to drought, capable of controlling soil erosion, and because of its widespread use for grazing in tropical countries.

Figure 11 shows the research development diagram outlining the delimitation of this study.

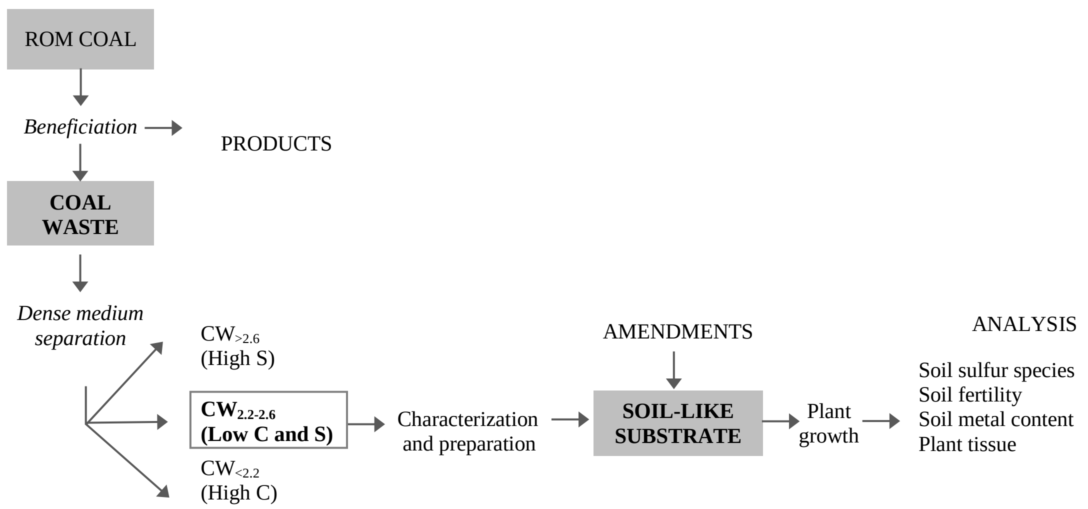

Figure 11. Research development diagram.

Results and Discussion

Results of the density separation tests indicate that 13 % of the coarse coal discards had a density of less than 2.2 g cm^{-3}, 68 % had a density between 2.2 and 2.6 g cm^{-3}, and 19 % had a density greater than 2.6 g cm^{-3}. Results for the characterization (proximate and elemental analysis, forms of sulfur and crystalline compounds) of bulk discards and three density fractions obtained after dense medium separation are shown in Table 10.

Table 10. Results of the proximate and elemental analysis, forms of sulfur and crystalline compounds in samples of raw coal waste and densimetric fractions obtained.

	Raw Coal Waste	$CW_{<2.2}$	$CW_{2.2\text{-}2.6}$	$CW_{>2.6}$
Weight (%)	100	13	68	19
Proximate analysis (%)				
Ash	78.6	62.3	83.1	73.7
Volatile matter	12.6	9.5	7.9	31.4
Fixed carbon	3.2	8.6	0.9	7.8
Elemental analysis (%)				
C	8.7	34.2	4.1	8.0
H	1.2	2.9	1.2	0.6
N	0.3	0.7	0.2	0.2
S	7.9	1.8	0.8	37.5
Forms of sulfur (%)				
Pyritic sulfur	6.8	1.3	0.5	32.8
Sulfate sulfur	0.1	0.2	0.1	0.4
Organic sulfur	1.1	0.3	0.2	4.9
Crystalline compounds				
Major		Carbonaceous matter	Quartz	Pyrite
Minor		Gypsum, Kaolinite, Jarosite	Plagioclase, Ilite Kaolinite, Feldspar	Quartz, Gypsum

As a waste management strategy, it is advisable to find uses for each coal waste fraction in accordance to its characteristics. The low density fraction ($CW_{<2.2}$) is rich in carbon (34.2 %) which is reflected by a lower ash content. When compared to a good quality thermal coal, the low density fraction has a higher ash content, however, previous studies have demonstrated the feasibility of co-combusting it with other materials to produce energy (Li et al., 2011, 2006; Muthuraman et al., 2010). Most (~ 91 %) of the pyritic sulfur in the feed is found in the high density fraction ($CW_{>2.6}$). This fraction had a pyritic sulfur content of 32.8 %, equivalent to 61 % pyrite, which allows sulfuric acid production via a pyrite roasting process (Chepushtanova and Luganov, 2007; Runkel and Sturm, 2009).

The intermediate fraction ($CW_{2.2\text{-}2.6}$) had the least carbon (4.1 %) and total sulfur (0.8 %) contents among all three fractions. Although comprising the bulk of the discarded material (68 % by mass) there are no large-scale uses established. Its pyritic sulfur content was relatively low (0.5 %), amounting to less than 5 % of the pyritic sulfur in the feed discards, meaning that it is capable of generating ARD over the long-term, however at a reduced rate (do Amaral Filho, 2017). Thus, it is important to control acid formation and find a suitable use for this fraction as a waste management strategy - in the case of the present study, as the main component of a coal derived soil-like substrate (SLS).

The interaction between $CW_{2.2\text{-}2.6}$, sewage sludge, steel slag and rice husk ash can be observed via plant growth. Figure 12 shows *M. maximus* height 100 days after planting. All plants grew taller than 50 cm without indications of nutrient deficiencies in plant tissue. Table 11 shows the results of dry mass and the percentage of total sulfur in root and aerial plant tissue; all results are expressed in terms of g kg^{-1} of soil. Mean values of dry mass were 20.8 g, with 14.5 g and 6.3 g, respectively, for aerial and root tissues. Average values of total sulfur were 0.2 % for aerial parts and 0.4 % for roots. Costa et al. (2005) and Aguiar (2004) found similarly equivalent aerial sulfur contents (0.14 to 0.16 %, and 0.07 to 0.18 %, respectively) after cultivating *M. maximus* in natural soil.

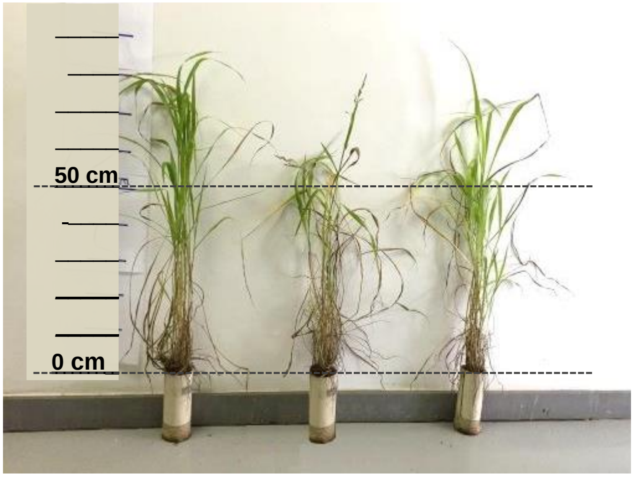

Figure 12. Soil-like substrate and M. maximus height 100 days after seeding.

Table 11. M. maximus dry matter 100 days after planting.

	Dry mass (g kg^{-1} of soil)		S-total (%)	
	Mean	SD*	Mean	SD*
Aerial	14.53	2.45	0.15	0.03
Roots	6.29	0.43	0.38	0.11
Total	20.82	2.86		

*SD – standard deviation

Table 12 shows the percentage of sulfur species (S-total, $S\text{-}SO_4$, $S\text{-}FeS_2$, S-organic) in the SLS, before and after planting. Results for total sulfur content indicate almost the same concentration before and after *M. maximus* growth, showing minimum addition of sulfur via irrigation and losses via leaching or plant absorption.

However, even though results show that total sulfur content didn't change, sulfur speciation did. Data indicate that SLS mixtures experienced a reduction of 50 % in their S-FeS_2 content during *M. maximus* growth, having been converted into S-SO_4 (9 % increase) and S-organic (50 % increase) after 100 days. This is consistent with the exposure of pyrite to an oxidizing environment (water and oxygen), soil microbial activity, and organic acids secreted by roots.

Table 12. Soil-like substrate sulfur speciation and Acid Base Accounting (ABA) parameters before and after plant growth.

	Before planting		After planting	
	Mean	Std Deviation	Mean	Std Deviation
Sulfur speciation (%)				
S-SO_4	0.31	0.05	0.37	0.06
S-FeS_2	0.63	0.25	0.32	0.08
S-Organic	0.48	0.20	0.80	0.03
S-Total	1.42	0.06	1.41	0.12
ABA parameters (kg $CaCO_3$ t^{-1})				
AP	19.63	-	9.54	-
NP	30.38	-	16.45	-
NNP	10.75	-	6.42	-

In terms of sulfur balance, data show that SLS had sulfur "inputs" from rain water and irrigation while plant tissue performed as an "output." Specifically, rain water added 0.13 g of sulfur per kilogram of soil while irrigation added an extra 0.15 g (0.28 g in total). Since sulfur corresponds to 33.33 % of the sulfate molecule, rain and irrigation water contributed 0.092 g kg^{-1} of sulfur to the soil over 100 days. During the same time period, above and below ground plant tissue removed 0.047 g of sulfur per kilogram of soil, accounting for only 0.33 % of total sulfur present in the soil. Figure 13 indicates the percentage of sulfur species before and after planting.

Both acid potential (AP) and neutralization potential (NP) of SLS were consumed during 100 days of *M. maximus* cultivation. AP was reduced from 19.63 to 9.54 kg $CaCO_3$ t^{-1} and NP, from 30.38 to 16.45 kg $CaCO_3 \cdot t^{-1}$ after 100 days, maintaining approximately the same proportion but with decreased potential reactivity.

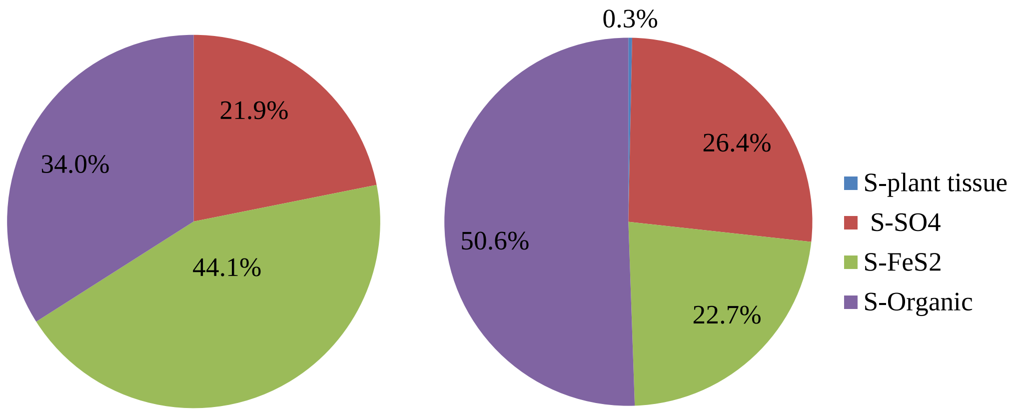

Figure 13. Sulfur speciation before and after planting.

Fertility parameters for SLS 100 days after *M. maximus* growth are shown in Table 13 along with the southern Brazilian soils' standard classification (CQFS - Núcleo Regional Sul, 2004). Clay content is very low and could lead to water supply limitations during drought periods. Soil pH (5.0) was lower than expected, but not enough to compromise nutrient supply or cause aluminum dissolution - an aluminum soil concentration above 2.0 $cmol_c \cdot kg^{-1}$ of soil is known for causing root toxicity in most plants and must be avoided. In order to maintain dense vegetation growth, soil pH should be higher than 5.0 and lower than 7.0; under that condition, pyrite oxidation depends mostly on water and oxygen activity known as the 'direct pyrite oxidation reaction.' This reaction is quite slower than 'indirect pyrite oxidation' led by Fe^{3+} in solution and supported by iron-oxidizing prokaryotic activity (e.g., *Acidithibacillus ferrooxidans*) below pH 4.5 (Kontopoulos, 1998; Baker and Banfield, 2003; Evangelou and Zhang, 1995; Singer and Stumm, 1970). Slow pyrite oxidation allows geochemical and biological transformation to sulfur species compatible with plant growth and microorganism uptake. An SMP Index of 7.0 and a potential acidity (H+Al) of 1.7 $cmol_c$ dm^{-3} indicate that soil pH is not buffered. Also, results show high cation exchange capacity (CEC) indicating a very good capacity to hold nutrients and avoid leaching losses as long as pH is kept circumneutral. Base (V%) and aluminium (m%) saturation values indicate that CEC sites are mainly occupied by basic cations that are good in terms of fertility.

As for nutrient supply, macro (Ca, Mg, P, and K) and micro (Zn, Cu, B, and Mn) nutrients were present and available in concentrations above critical levels indicating that no further fertilization was necessary. Sulfur, also a nutrient, was very high mainly due to the use of coal waste and sewage sludge. Results are consistent with the raw material composition: phosphorus and organic matter (3.3 %) were added by sewage sludge; potash and sulfur added through coal waste; calcium, magnesium, copper, boron and manganese by steel slag.

Table 13. Fertility parameters for soil-like substrate after plant growth.

	Mean	Std	Classification CQFS (2014)
Clay (%)	9.3	1.5	class 4
pH H_2O (1:1)	5.0	0.5	low
SMP Index	7.0	0.6	-
$Al_{exch.}$(cmol$_c$ dm^{-3})	0.0	0.1	-
Al+H (cmol$_c$ dm^{-3})	1.7	1.2	-
CEC (cmol$_c$ dm^{-3})	44.3	3.3	high
Base saturation - V%	96.3	2.9	eutrophic
Al saturation - m%	0.0	0.1	-
$Ca_{exch.}$ (cmol$_c$ dm^{-3})	32.4	4.8	high
$Mg_{exch.}$ (cmol$_c$ dm^{-3})	9.9	0.9	high
P (mg dm^{-3})	71.3	10.4	very high
K (mg dm-3)	112	15.1	high
S (mg dm^{-3})	1747	158	high
Zn (mg dm^{-3})	56.7	17.0	high
Cu (mg dm^{-3})	6.7	0.5	high
B (mg dm^{-3})	0.5	0.3	high
Mn (mg dm^{-3})	20	15.7	high
Organic matter (%)	3.3	0.3	medium

Clay content (clay densimetric method); pH (pH_{H2O} 1:1); lime requirement (Shoemaker-McLean-Pratt - SMP buffer method); P and K (Mehlich 1); organic matter (humid digestion), exchangeable Ca, Mg, Al and cation exchange capacity - CEC (KCl 1 mol L^{-1} extraction); Cu, Zn, and Mn (HCl 0,1 mol L^{-1} extraction); S-SO_4 ($CaHPO_4$ 500 mg L^{-1} of P); B (hot water extraction).

A lack of natural soils for mining restoration is a reality for some coal mining sites, thus alternative substrates are welcome. If approached carefully, coal mine wastes can be successfully processed and combined with other products in order to produce suitable topsoil substitutes while preserving natural ones (Darmody et al., 2009; Liu and Lal, 2014; Schoeman and van Deventer, 2004; van Deventer and Hattingh, 2004). Large scale pyrite removal can be carried out in conventional rock processing equipment such as jigs or dense-medium cyclones followed by comminution and classification operations with crushers, mills and screens (Leonard, 1979). It is advisable to integrate waste management into the operational framework (Komnitsas et al., 2001). In this manner, coal wastes could be processed in the preparation plant avoiding unnecessary loading and unloading operations and exposure to weathering in piles which would ultimately lead to pyrite oxidation with unavoidable and undesirable enrichment in sulfur of the $CW_{2.2-2.6}$ fraction. It must be recognized that different parent materials and local conditions have led to multiple and unique results under site-specific situations as in the present study (Askenasy et al, 1997; Orndorff et al., 2010; Sheoran et al., 2010).

Parallel to the direct benefits of a coal derived soil-like substrate use (like avoiding waste accumulation and the use of natural soils for environmental reclamation) there are indirect benefits related to carbon sequestration that can happen through soil organic matter (SOM) accumulation over time. Since SOM is mainly comprised of carbon, nitrogen, phosphorus, and sulfur, mine soils (usually low in SOM) are an opportunity for both sulfur and carbon sequestration (Kirkby et al., 2011; Shrestha and Lal, 2006; Stahl et al., 2003; Ussiri and Lal, 2005; Vindušková and Frouz, 2013). SOM is responsible for nutrient cycling, water holding capacity, and soil structure among other characteristics. Also, approximately 90 % of the total S in soils is found in soil organic matter (Mengel and Rehm, 2000). This study contributes to the value of proper waste management linking desulfurized coal waste to amendments (wastes as well) as a promising coal waste derived soil-like substrate (SLS) and should be seen as an integrated part of the mining process.

Conclusion

Growing *Megathyrsus maximus var. maximus* (Guinea grass) in a soil-like substrate (CW-SLS) composed of desulfurized coal waste amended with sources of alkalinity (steel slag), organic matter (sewage sludge), and soil physical conditioner (rice husk ash) is feasible and is supportive of the idea of the transformation of wastes into soils. The system showed a 50 % reduction in S-FeS_2, an increase of S-organic and a good potential for using the proposed SLS as topsoil. The development of an SLS in coal mining scenarios can help reduce environmental impacts associated with coal waste, steel slag, sewage sludge and rice husk ash disposal, and will also avoid additional impacts from deforestation and landscape changes where natural soils are borrowed for mining reclamation activities. Future research should focus on sulfur bioaccumulation by plants, other plant species, alternative organic carbon and alkalinity sources, and long term cultivation.

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PARTE III

6. CONSIDERAÇÕES FINAIS

A região carbonífera de SC gera grandes volumes de rejeitos de carvão que estão associados a pirita (FeS_2), podendo dar origem à drenagem ácida de minas (DAM). Por muitos anos, a disposição dos rejeitos foi realizada de forma imprópria e com descaso à formação da DAM, impactando muitas áreas e corpos hídricos da região. Embora atualmente existam sistemas de coleta dos lixiviados e de tratamento da DAM, essa técnica não retrata a atual tendência de reuso de resíduos sólidos e é insustentável em casos de longos períodos de geração da DAM. A possibilidade de processar o rejeito para permitir seu uso, de forma a evitar que os mesmos sejam dispostos em superfície, aparece como uma opção preventiva e ambientalmente preferível dentro dos preceitos de sustentabilidade no gerenciamento de resíduos sólidos.

A alternativa abordada nos estudos que compõem essa tese contempla a separação por meio denso dos rejeitos para concentração da pirita, restando um material inerte, com baixo potencial de geração de DAM. A técnica mostrou-se passível de ser aplicada e adequada para redução da DAM, possibilitando o uso dos rejeitos para outros fins. Focou-se nos ganhos do uso da pirita, como matéria prima para produção de ácido sulfúrico, e da fração dessulfurizada, para manufatura de um tecnossolo com capacidade de iniciar e sustentar o crescimento vegetal em um processo de recuperação ambiental.

Avaliando um cenário de aplicação do meio denso aos rejeitos produzidos na região carbonífera de SC, estimou-se que seriam produzidos 578.900 ton ano^{-1} de um concentrado pirítico com um teor médio de pirita de 58,2%, equivalente a 539.245 ton ano^{-1} de ácido sulfúrico, produção atualmente inexistente no sul do país, ou um equivalente a enxofre elementar que corresponderia a um aumento de 25% na produção brasileira desse insumo.

Testes estáticos de predição de DAM mostraram uma redução de quase 90% no potencial de geração de acidez dos rejeitos em relação à fração dessulfurizada, enquanto os ensaios cinéticos em células úmidas mostraram que os lixiviados do rejeito dessulfurizado apresentam redução no teor de Fe (60%), Al (54%), Zn (48%), sulfato (51%) e acidez (55%), e ainda, metade da taxa de oxidação da pirita. Isso facilitaria o tratamento e diminuiria o tempo de geração da DAM nos módulos de rejeitos, caso o rejeito fosse disposto de tal maneira.

A partir dos resultados apresentados para a fração com reduzido teor de enxofre e menor geração de DAM, um terceiro estudo foi produzido mostrando a utilização dessa fração como matriz mineral em substratos para crescimento vegetal, juntamente com lodo de estação de tratamento de esgoto (material orgânico), escória de aciaria (alcalinidade) e cinza de casca de arroz (estrutura física). Além do crescimento satisfatório da *Megathyrsus maximus var. maximus* (*Guinea grass*), houve alteração na especiação do enxofre, com redução de 50% no teor de enxofre pirítico e de geração de acidez dos rejeitos após plantio. O tecnossolo produzido tem potencial para ser usado como solo de cobertura nas próprias áreas mineradas, reduzindo a necessidade de solos de áreas de empréstimo e permitindo a revegetação dos locais degradados.

Por fim, o estudo considera que a aplicação da metodologia é adequada para o aproveitamento integral de rejeitos, abordando conceitos de conservação ambiental, redução de matéria prima e incorporação de resíduos sólidos de outros setores. Essa concepção contrapõe o antigo processo utilizado na mineração de carvão, que adota uma linha de produção linear e com sistemáticas de controle da poluição considerados “fim-de-tubo”, e conduz o setor a atual tendência da economia circular.

7. SUGESTÕES PARA TRABALHOS FUTUROS

Aplicação da metodologia de isolamento de sulfetos a rejeitos de mineração de jazidas de sulfetos polimetálicos, tal como a mineração de Pb, Zn e Cu.

Em relação à fração pirítica: avaliar reações e rotas para obtenção de produtos tais como sulfato férrico, sulfato ferroso e pigmentos, considerando eficiência operacional e questões técnico-financeiras.

Em relação aos Tecnossolos: investigar uso de diferentes espécies vegetais, tal como plantas acumuladoras de enxofre; avaliar outras fontes de carbono orgânico e alcalinidade; monitorando a microbiologia do solo; testar inoculação de microrganismos; análise de transformações do carbono orgânico e matéria orgânica; e realizar cultivos de longo prazo.