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CO_2矿化研究现状及应用潜力

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摘　要：CO_2浓度急剧上升成为一个很严峻的问题，因此，降低大气CO_2浓度成为当务之急．目前涉及的方案中的海洋封存、地质封存，虽封存潜力巨大，但带来的负面影响也不容小觑．CO_2矿化利用实质是模拟自然界岩石化学风化，作为一种新兴的减排方案，既能固定大气CO_2，生成具有工业附加值的碳酸盐产品，又能实现环境友好．能够矿化利用的原材料包括天然富钙、镁硅酸盐矿物，工业碱性废固、液，盐湖中的氯化镁资源等，矿化利用的方法也不尽相同．虽然硅酸盐岩的风化是如何控制长时间尺度的气候变化的机制还没有定论，但风化过程中具有固定大量CO_2的潜力这一认识已达成共识．对含有大量硅酸盐矿物的尾矿矿化CO_2的研究是目前的热点，介绍了尾矿矿化CO_2的研究现状及几种重要尾矿矿物的矿化应用潜力．

关键词：CO_2矿化；碱性矿物；工业废固；尾矿；碳酸化反应；矿物学．

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Research Status and Application Potential of CO_2 Mineralization

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Abstract: The sharp rise of carbon dioxide concentration has become a very serious problem, so reducing the atmospheric carbon dioxide concentration has become a top priority. Although the potential of marine and geological sequestration is huge, the negative impact of these schemes can not be underestimated. As a new emission reduction scheme, carbon dioxide mineralization can not only fix atmospheric carbon dioxide, generate carbonate products with industrial added value, but also achieve environmental friendliness. Raw materials that can be used for mineralization include natural calcium-rich, magnesium silicate minerals, industrial alkaline waste solids, liquids, magnesium chloride resources in salt lakes, etc. The methods of mineralization are also different. Although the mechanism of how the weathering of silicate rocks can control the long-term climate change has not been determined, there is a consensus that the weathering process has the potential to fix a large amount of CO_2. The research on the mineralized CO_2 of tailing containing a lot of silicate minerals is a hot spot at present. This paper introduces the research status of mineralized CO_2 of tailing and the mineralized potential of several important tailing minerals.

Key words: CO_2 mineralization; alkaline minerals; industrial waste; tailings; carbonation reaction;mineral deposite.

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0 引言

大气CO_2作为一种能吸收热量的温室气体在很大程度上驱动地球气候变化（Neftel *et al.*, 1982; Etheridge *et al.*, 1996; Petit *et al.*, 1999; Han *et al.*, 2018; Brame *et al.*, 2019; Fang *et al.*, 2019）.工业革命以来，化石燃料的大量使用打破了地质历史时期上CO_2的动态平衡，引发了诸多环境问题，减排CO_2已成为全球性热议话题（谢和平，2010；谢和平等，2012；Xie *et al.*, 2014）.尽管各国都在积极开发太阳能、核能、生物质能等新能源，但是化石燃料目前仍然占据能源消耗结构中的主体地位，这意味着环境恶化状况会持续增加（崔振东等，2010）.因此，如何在末端处理化石能源燃烧所排放的CO_2已成为短期CO_2减排的主要方向．自从Marchetti（1977）首先提出将液态CO_2注入北大西洋中层水体的构想之后，CO_2捕捉封存技术成为全世界各国研究的热点．为了提高CO_2减排的经济性，我国科学家提出了CO_2捕捉利用和封存的减排思路（谢和平等，2012）.

CO_2封存技术被认为是最有潜力的减排CO_2的手段，具有以下优点：封存场所包括海洋或峡湾深部（Smith *et al.*, 2015; Cui *et al.*, 2016; Zimmerman and Cornelissen, 2018），也包括了一些地质体，例如：地壳深部沉积地层和咸水层、废弃的油气藏、不可开采的煤层、超基性岩体（Holloway, 1997; Goff and Lackner, 1998; Bachu and Adams, 2003; Lokhorst and Wildenborg, 2005; 周军平等，2010; Gislason and Oelkers, 2014; Romanov *et al.*, 2015; 杜玉昆等，2019）等，能够实现大规模封存，使被封存的CO_2与大气长期隔离．之后有研究表明，该方法存在有许多潜在风险，如破坏生态平衡，或在局部地区引发CO_2泄漏、诱发地震、造成地表拱起、咸水层破坏（谢和平等，2012；Zoback and Gorelick, 2012；李琦等，2019；Suarez *et al.*, 2019）等（图1）.

因此Seifritz（1990）提出矿物碳酸化反应．接着Lackner（1995）提出矿物储存CO_2，又称为CO_2矿化利用．该方法相对于CO_2地质封存和海洋封存方式最大的区别在于能够将CO_2固定在稳定的生成物中．CO_2矿化作用的本质为模拟自然界天然岩石的化学风化过程，利用含有钙镁元素的矿物将CO_2矿化为稳定的固体碳酸盐，从而实现CO_2的减排（Seifritz, 1990; Lackner *et al.*, 1995; Gerdemann *et al.*, 2007）.其示意图如图2.

1 CO_2矿化原料

从化学角度分析，含有碱性元素的矿物都可以作为CO_2矿化的原材料．目前对于矿化原料的选择主要集中在工业废固、液（碱性）和天然碱性岩石中．常见的工业废固有：市政固体焚烧炉底灰、建筑废弃物、钢渣、富含钙镁的工业废弃物、空气污染控制残留物、电站燃煤产生的废料、水泥窑粉尘、燃煤灰尘、赤泥等（Lizuka *et al.*, 2004; Stolaroff *et al.*, 2005; Baciocchi *et al.*, 2006; Huijgen *et al.*, 2006; Teir *et al.*, 2007; Lekakh *et al.*, 2008; Huntzinger, 2009; Huntzinger *et al.*, 2009; Montes-Hernandez *et al.*, 2009; Uibu *et al.*, 2009；Katsuyama and Yamasaki, 2010；Yadav *et al.*, 2010；唐海燕等，2014；谢和平等，2014）.这些工业废固、液中含有大量的钙镁金属离子，可将CO_2固定为碳酸镁和碳酸钙等稳定的碳酸盐．虽然碱性工业废固、液具有较高的反应活性，可作为理想的矿化原料，然而其

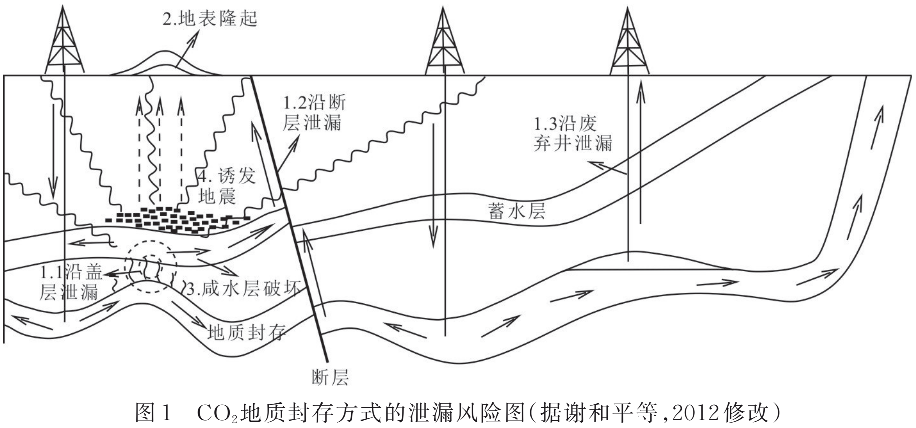

图1 CO_2地质封存方式的泄漏风险图（据谢和平等，2012修改）

Fig.1 Leakage risk map for CO_2 geological storage(modified from Xie *et al.*, 2012)

总量相对于天然碱性岩石要少得多(唐亮，2017).

自然界中富含钙镁离子的岩石被认为是重要的矿化原料具有大规模减排CO_2的潜力(Macdonald *et al.*, 2009; Sanna, 2014). 目前用于矿化研究的主要有橄榄石、蛇纹石、硅灰石等(Lackner *et al.*, 1995; Huijgen *et al.*, 2006; Gerdemann *et al.*, 2007; Hanchen *et al.*, 2008；张兵兵等，2012; Olajire, 2013). 该类岩石的主要化学成分为硅酸钙和硅酸镁，反应通式为：$(Mg,Ca)_xSi_yO_{x+2y}+xCO_2 \rightarrow x(Mg,Ca)CO_3+ySiO_2$(王宗华等，2008)，用于矿化$CO_2$，既可实现固定$CO_2$，又可产出高附加值的碳酸盐产品(表1).

表 1　用于矿化的工业废固、液主要成分及其反应方程式

Table 1　Main compositions of industrial waste solids and liquids for mineralization and their reaction equations

矿化原料	矿化的主要化学成分	化学方程式
石灰窑粉尘	CaO、MgO	$CaO+CO_2 \rightarrow CaCO_3$ $MgO+CO_2 \rightarrow MgCO_3$
煤粉灰	CaO	$CaO+CO_2 \rightarrow CaCO_3$
钢渣	CaO、MgO	$CaO+CO_2 \rightarrow CaCO_3$ $MgO+CO_2 \rightarrow MgCO_3$
电石渣	$Ca(OH)_2$、$Mg(OH)_2$	$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O$ $Mg(OH)_2+CO_2 \rightarrow MgCO_3+H_2O$
白泥	$Ca(OH)_2$、$Mg(OH)_2$、CaO	$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O$ $Mg(OH)_2+CO_2 \rightarrow MgCO_3+H_2O$ $CaO+CO_2 \rightarrow CaCO_3$
盐泥	$Mg(OH)_2$	$Mg(OH)_2+CO_2 \rightarrow MgCO_3+H_2O$
电石废水	$Ca(OH)_2$	$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O$
纺织、印染废水	$NaOH$	$NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$
盐湖苦卤	$MgCl_2$	$2NH_3 \cdot H_2O+CO_2 \rightarrow (NH_4)_2CO_3+H_2O$ $MgCl_2 \cdot 6H_2O+(NH_4)_2CO_3 \rightarrow MgCO_3 \cdot 3H_2O+2NH_4Cl+3H_2O$ $5MgCl_2 \cdot 6H_2O+5(NH_4)_2CO_3 \rightarrow Mg(OH)_2 \cdot 4H_2O+10NH_4Cl+CO_2+26H_2O$
磷石膏	$CaSO_4 \cdot H_2O$	$CaSO_4 \cdot H_2O+2NH_3 \cdot H_2O+CO_2 \rightarrow (NH_4)_2SO_4+CaCO_3+3H_2O$

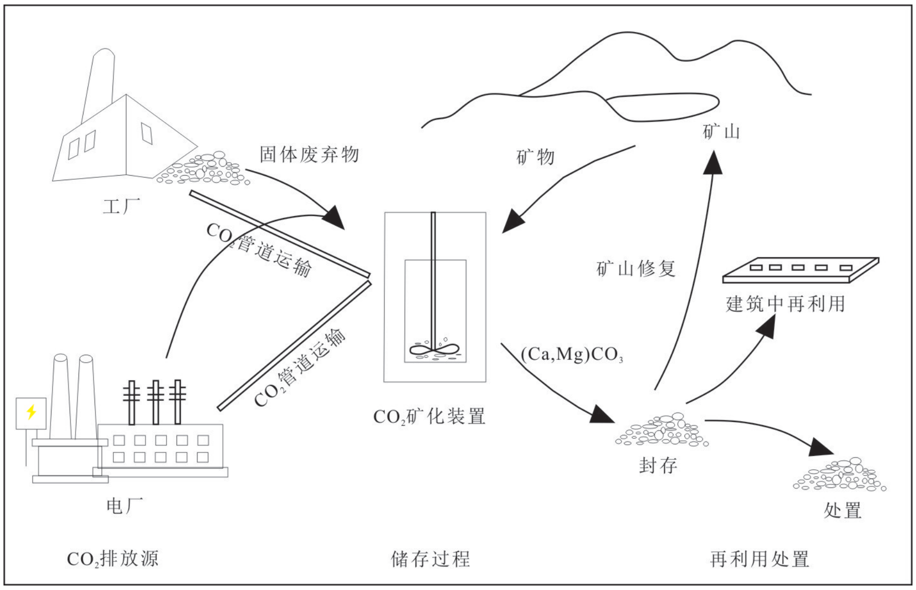

图 2　CO_2矿化封存示意图(Metz *et al.*, 2005)

Fig.2　Schematic of a CO_2 mineral carbonation operation(modified from Metz *et al.*, 2005)

橄榄石是最具意义的CO_2矿化原料．使用橄榄石作为矿化CO_2具有以下几个优点，包括：广泛分布于全球，有大量橄榄石可用于矿化人类作用排放的CO_2（盛雪芬等，2011；Olsson *et al.*，2012）；在钒、钛、磁铁矿，铜、镍和金刚石等多种矿床中，橄榄石在尾矿中占了很大比例（Kelemen and Matter，2008；Meyer *et al.*，2014）．蛇纹石是另一种富镁硅酸盐矿物，多由橄榄石受热液作用蚀变而成，两者成分相似．我国蛇纹岩矿产资源十分丰富，大都是超基性岩类型的蛇纹岩矿床，具有矿床多、规模大、分布广等特点（刘振敏和吴颖慧，2015），因此蛇纹石也可为CO_2矿化的原材料（高雄等，2011；高雄等，2012），其反应机理与橄榄石相似（晏恒等，2013）．硅灰石是一种活性矿物，在很多化学工业中，纯的硅灰石矿物被认为是一种具有经济价值的原料（Liu *et al.*，2004）．我国的硅灰石储量大约为1万亿吨，2004年产量约占世界总产量的53%（潘霞，2007），大量硅灰石存在于矽卡岩、斑岩、接触交代矿床等尾矿中（赵一鸣等，2017）．水镁石为热液接触反应的产物，与蛇纹石、方镁石、方解石等矿物共生，具有天然碱性（Hovelmann *et al.*，2012）．水镁石比橄榄石、蛇纹石具有更好的反应活性，因此，近年来水镁石成为矿化CO_2的研究焦点（Zhao *et al.*，2010；Schaef *et al.*，2011）．

2 CO_2矿化工艺

根据矿化反应过程可将CO_2矿化反应分为直接矿化法和间接矿化法．直接矿化法是利用矿化原料与CO_2进行一步碳酸化反应，得到碳酸盐产物；间接法是指先用某种媒介将矿化原料转化为中间产物，然后与CO_2发生反应，最终生成固体碳酸盐．

直接法分为直接干法和直接湿法．直接干法工艺简单，即使用矿化原料与CO_2气体直接接触反应，然而常温常压下反应速率缓慢（Lackner *et al.*，1997）．通过对硅酸盐矿化活性的研究，只有经过650℃高温活化后，才能与CO_2发生直接反应（Maroto-Valer *et al.*，2005）．升高反应体系温度会促进反应的进行，但是不利于反应的平衡，反应流程如图3．直接湿法是利用CO_2溶于水形成碳酸，然后再与矿化原料反应（O'Connor *et al.*，2000）．该法与直接干法相比，明显地提高了反应速率．然而该方法只适用于反应活性较高的工业废固，在天然矿石矿化的应用中，成本过于高昂（O'Connor *et al.*，2004）．因为在直接碳酸化过程中，随着硅酸盐矿物的碳酸盐化，会逐渐积累无定形二氧化硅的钝化层附着在反应物表面阻碍金属离子的浸取（Daval *et al.*，2011；King *et al.*，2014），进而影响碳酸化反应的进程．

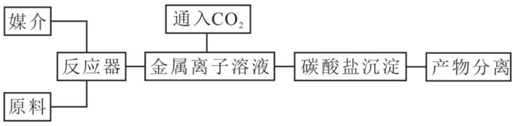

图3 直接干法矿化反应流程示意图

Fig.3 Diagram of direct dry mineralization reaction flow

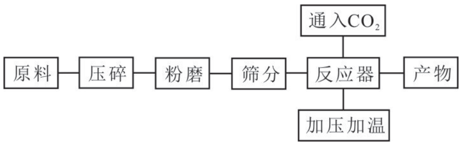

图4 间接湿法矿化反应流程示意图

Fig.4 Indirect wet mineralization reaction flow chart

间接矿化法即选取一种合适的物质作为反应媒介，旨在提高碳酸化的反应活性，从而提高反应速率与转化率（流程如图4）．目前可供间接法反应选取的媒介多为常见的酸溶液或碱溶液以及铵盐溶液（Zhang *et al.*，2012；Steel *et al.*，2013；Wang and Maroto-Valer，2013；Hemmati *et al.*，2014）．Lackner *et al.*（1995）首先提出基于盐酸的反应路线，可概括为先用盐酸浸出矿物中的金属离子，然后电解金属氯化物熔盐生成氢氧化物，最后再通入CO_2气体生成碳酸盐沉淀．该方法能耗较高，而且会造成氯的损耗，导致成本高昂．在上述方法基础之上，有学者提出利用金属氯化物熔盐代替盐酸的方法（Wendt *et al.*，1999）．此举有降低能耗的优点，但还是难以弥补氯化物的损耗，因此，很难实现工业化．Kakizawa *et al.*（2001）提出以乙酸为媒介的反应路线，乙酸较盐酸酸性较弱，回收循环利用相对容易，又利于降低能耗．但由于乙酸会溶解已生成的碳酸盐沉淀，导致该方法的实验转化率远低于理论转化率．Blencoe *et al.*（2004）提出以NaOH为媒介的反应路线．该方法不需预先活化处理原材料，降低了反应能耗，然而该方法对碱的需求量过大，而且反应时间长，产物分离困难．

3 CO_2矿化机理

CO_2中的碳元素和碳酸盐化合物中的碳元素均

处于最高价态，根据其标准吉布斯自由能，碳元素的最终稳定形态应为碳酸盐．CO_2与硅酸盐岩发生反应为放热反应，相比于其他CO_2储存方法，CO_2矿化具有以下优点（徐俊，2006；王宗华等，2008）：天然碱性硅酸盐岩储量丰富，易于开采，可实现大规模的CO_2处理；矿物碳酸化产物为稳定的碳酸盐，环境污染小且能够永久封存CO_2；矿物碳酸化为放热反应，具有商业化应用潜力．自然条件下，天然岩石与CO_2的反应速率极为缓慢，探索一种矿化CO_2速率更快、固定率更高的、生成物稳定、经济上可行的方法成为目前研究的核心内容．

对于矿物与CO_2的反应分为两步：首先是使矿物中金属离子的溶解，$Ca/Mg\text{-}silicates(s)+2H^+(aq)\rightarrow(Ca/Mg)^{2+}(aq)\rightarrow SiO_2(s)+H_2O$（吴昊泽，2011）；其次是生成碳酸盐沉淀，其中金属离子的溶解过程决定整个反应的速率（王昱飞，2015）．Huijgen *et al*.（2006）研究了不同条件下长石的溶解速率，得到了酸性越强，越容易溶解、CO_2几乎不影响溶解效果两条结论．Alexander *et al*.（2007）研究了常温下多种基性岩在不同pH值下的溶解速率，结果表明溶解速率随着酸性的增强逐渐增加，但速率的增长幅度逐渐减小，并得出CO_2的存在几乎不影响溶解效果的结论．仅仅使用酸溶液浸出矿物中金属离子最大的缺点是酸碱损耗过大，导致成本高昂．反应体系的pH值和CO_2的分压对产物的分离起着至关重要的作用．

目前，针对橄榄石、蛇纹石矿化方法多采用电解NaCl促进方式（Berndt *et al*., 1996；李文志等，2007；李文志等，2010；张建树等，2011）．首先电解NaCl溶液生成NaOH和HCl，利用HCl浸取橄榄石、蛇纹石中的金属离子形成镁离子溶液，再利用NaOH吸收CO_2形成$NaHCO_3$溶液，在一定条件下将两种溶液混合形成$MgCO_3$沉淀．该类反应主要消耗能量为电解NaCl过程，其他反应步骤虽为放热反应却很难加以利用，因此不能抵消电解消耗的能量．反应最终产物为可作为工业应用的碱式碳酸镁．此外，CO_2和橄榄石反应的$\triangle Gr^0$为负值，所以该反应可自发进行，虽然在常温下和大气中CO_2反应缓慢（Mckelvy *et al*., 2003；Schuiling and Krijgsman, 2006；Peuble *et al*., 2015），但利用细粉状橄榄石在农田、林地和土壤中吸收CO_2也被广泛研究（Huijgen *et al*., 2006；Miilar *et al*., 2015；Monger *et al*., 2015），其积极意义不亚于实验室的橄榄石与CO_2反应．硅灰石在矿化过程中多为直接利用酸溶液浸取金属离子然后与CO_2进行反应形成碳酸钙沉淀，且浸取金属离子的酸多为弱酸（张军营等，2008；朱辰等，2011）．水镁石的矿化一般采用氯化铵作为反应介质，铵根离子水解可产生酸性环境，有利于将矿物中镁离子浸出从而进行碳酸化反应（Rendek *et al*., 2006）．

影响矿化反应的因素主要有：原料粒径大小、反应温度、压力等，为了更好地提高矿化反应的速率以及转化率，对这些影响因素的研究十分有必要．原料粒径大小对原料的溶解起决定性作用，进而决定整体反应的进程，反应速率一般随原料粒径增大而降低．O′Connor *et al*.（2000）研究减小粒度对反应速率的影响，当粒度从150 μm减小到37 μm，转化率可以从10%增加到90%．反应物中的酸性物质浓度不宜过大，否则会分解已生成的反应产物．温度不仅可以影响反应平衡，还会导致生成物成分出现差异（表2）．

4　尾矿在CO_2矿化中的作用

当今，全球碳循环面临着一个主要问题就是全球CO_2收支不平衡，存在一个较大的遗漏汇（Broecker *et al*., 1979；Houghton *et al*., 1992；Joos, 1994；Houghton *et al*., 1999；袁道先，2001；Black and Gibson, 2019）．一般而言，碳从什么地方来最终会经历各种循环过程回到原处，使得碳在地球系统中保持着相对平衡态（Suarez *et al*., 2019）．学术界认为一些地质作用参与了短时间尺度内的全球碳循环，如CO_2浓度升高使岩溶作用更活跃，从而吸收更多大气中的CO_2（翁金桃，1995；姚锐，2003；刘再华等，2011；刘再华，2012；Li *et al*., 2017, 2018, 2019；倪健，2017；王世杰等，2017；曾庆睿和刘再华，2017；李汇文等，2019；李朝君等，2019）．然而，碳酸盐岩溶解过程中消耗的所有二氧化碳又通过海洋中相对快速的碳酸盐沉积而返回大气（Kasting, 1984；Elderfield, 2010；Izumi *et al*., 2018）．硅酸盐岩吸收大气中CO_2并将其作为碳酸盐产物固定，存留时间超过百万年．硅酸盐矿物的溶解和矿山尾矿碳酸盐矿物的沉淀被认为是固定大气CO_2的一种潜在方式（Schwartzman and Volk, 1989；Kelemen and Matter, 2008；Tanaka *et al*., 2016；方谦等，2018）．研究表明，生物腐殖质、有机和无机酸、螯合剂（Schwartzman and Volk, 1989），

表2　不同矿化原料矿化反应方程式及最优条件

Table 2　Equations and optimum conditions for mineralization reaction of different mineralized raw materials

原料	媒介	方程式	最优条件
橄榄石	NaCl	$2NaCl+2H_2O \rightarrow 2NaOH+Cl_2+H_2$ $Cl_2(g)+H_2 \rightarrow 2HCl$; $4HCl+Mg_2SiO_4 \rightarrow 2MgCl_2+SiO_2+2H_2O$ $CO_2+NaOH \rightarrow NaHCO_3$; $MgCl_2+2NaHCO_3 \rightarrow MgCO_3+2NaCl+H_2O+CO_2$	粒径$<110\ \mu m$ $t=90$ ℃ 盐酸浓度<3 mol/L
蛇纹石	NaCl	$2NaCl+2H_2O \rightarrow 2NaOH+H_2+Cl_2$ $Cl_2+H_2O \rightarrow HCl+HClO$ $2HClO \rightarrow 2HCl+O_2$ $6HCl+Mg_3SiO_5(OH)_4 \rightarrow 3MgCl_2+2SiO_2+5H_2O$ $CO_2+NaOH \rightarrow NaHCO_3$ $MgCl_2+2NaHCO_3 \rightarrow MgCO_3+2NaCl+H_2O+CO_2$	$p=4$ MPa $t=150$ ℃ 粒径$<30\ \mu m$
硅灰石	HAc	$CaSiO_3+2H^+ \rightarrow Ca^{2+}+H_2O+SiO_2$ $CO_2+H_2O \rightarrow H_2CO_3 \rightarrow H^++HCO_3^-$ $Ca^{2+}+HCO_3^- \rightarrow CaCO_3+H^+$	$p=4$ MPa $t=150$ ℃ 粒径$<30\ \mu m$
水镁石	NH_4Cl	$Mg(OH)_2+2NH_4Cl \rightarrow MgCl_2+2NH_3+2H_2O$ $NH_3+H_2O \rightarrow NH_4OH$ $NH_4OH+CO_2 \rightarrow NH_4HCO_3$ $2NH_4HCO_3+MgCl_2+2H_2O \rightarrow MgCO_3\cdot 3H_2O+2NH_4Cl+CO_2$	粒径$<91\ \mu m$ $t=100$ ℃ 氯化铵3 mol/L
磷石膏	$NH_3\cdot H_2O$	$CaSO_4\cdot H_2O+2NH_3\cdot H_2O+CO_2 \rightarrow (NH_4)_2SO_4+CaCO_3+3H_2O$	$t=65$ ℃、 固液比3.0、 氮硫比2.25
氯化镁	$NH_3\cdot H_2O$	$2NH_3\cdot H_2O+CO_2 \rightarrow (NH_4)_2CO_3+H_2O$ $MgCl_2\cdot 6H_2O+(NH_4)_2CO_3 \rightarrow MgCO_3\cdot 3H_2O+2NH_4Cl+3H_2O$ $5MgCl_2\cdot 6H_2O+5(NH_4)_2CO_3 \rightarrow Mg(OH)_2\cdot 4H_2O+10NH_4Cl+CO_2+26H_2O$	$t=40$ ℃、 氯氨比1.0、乙醇体积分数30%

水合环境(Wilson *et al.*, 2009)和粒度大小(Vogeli *et al.*, 2011)大大加速了尾矿的固－液反应．在尾矿堆中发现碳酸盐矿物表明尾矿风化封存CO_2是一个较快的过程(李子波等,2011)．在铜锌矿尾矿(Al *et al.*, 2000)、铀矿尾矿(Paktunc and Davé, 2002)、纤蛇纹石尾矿(Wilson *et al.*, 2006)、及金伯利岩尾矿(Wilson and Dipple, 2009)中均发现有碳酸盐矿物沉淀．Wlison *et al.*(2006)、Rollo and Jamieson (2006)提出如果超基性岩尾矿中的碳酸盐矿物主要来自大气中的CO_2,那么超基性岩尾矿的风化就可以用来封存CO_2,而C与O同位素数据(Wilson and Dipple, 2009)表明这些镁碳酸盐矿物固定的CO_2直接来源于大气．

在利用尾矿进行CO_2矿化的研究上,国外学者进行得较早,也取得了较多的成果．通过对部分尾矿研究认识到尾矿矿化产物水合碳酸镁形成于两大环境中:(1)形成于尾矿堆表面蒸发环境中的碳酸镁石来自二氧化碳矿化;(2)形成于与土壤中碳酸盐有类似的地下环境中的水合碳酸镁,主要的矿物组成为钛铌钙铁矿和菱镁矿(Rollo and Jamieson, 2006; Wilson *et al.*, 2009)．尾矿中溶解的阳离子可以与溶解的无机碳(DIC,包括H_2CO_3,HCO_3^-,CO_3^{2-},CO_{2aq})达到化学平衡,尾矿的化学风化速率可直接反映CO_2矿化速率,并最终形成碳酸盐岩．钙离子多赋存于尾矿中的碳酸盐岩,碳酸盐岩在尾矿中占比较小,因此,碳酸盐岩对CO_2的封存贡献较小．与碳酸盐岩相比,钙在斜长石和辉石中富含活性,且具有矿化CO_2能力．简而言之,尾矿中的Ca储量的顺序为:斜长石>辉石>橄榄石>其他．橄榄石和辉石具有丰富的镁含量,Mg的风化速率高于Ca的风化速率,因此橄榄石和辉石对CO_2矿化过程具有重要意义．尾矿中斜长石、辉石和橄榄石具有较低的经济价值,可作为矿化CO_2的主要原料．

此外,利用尾矿矿化利用CO_2具有两大优势:尾矿具有颗粒小、比表面积大等特点,可降低矿化原料预处理的成本(唐亮,2017);可以改善生态环境,提高尾矿的价值．尾矿既是重大污染源,又是一种重要的矿产资源(刘志强等,2016),截至2014年,中国拥有超过12 655个尾矿坝(Yu *et al.*, 2014),这些都是CO_2封存的潜在物质源．因此,尾矿CO_2封存

是降低大气CO_2的可选择方式之一，通过尾矿中的富镁硅酸盐矿物与CO_2结合生成稳定的碳酸盐产物，实现CO_2的永久封存（李子波等，2011），其前景和实用性前途广泛．

5　结论

富含碱性金属离子（Ca^{2+}、Mg^{2+}）的天然岩石和工业废固、液理论上都可作为矿化CO_2的原材料．应用于矿化的原料要具有一定的反应活性，预处理的成本要尽可能的低（例如利用尾矿），矿化结果要做到有利于改善环境．

矿化工艺应选取间接湿法矿化，该工艺的矿化效率相对较高．影响CO_2矿化反应的因素有很多，如反应温度、反应压力、矿化原料颗粒大小等，考虑经济利益的前提下，找寻针对每种矿化原料最适宜的反应条件．矿化反应一般为放热反应，反应中的热量除抵消消耗的一部分外，其余热量的收集利用是现在的研究重点．

尾矿既是重要污染源，又是一种重要的矿产资源．通过尾矿中硅酸盐矿物与CO_2发生碳酸化反应，可实现CO_2的永久固定．尾矿中存在大量可用于矿化的钙、镁基资源，考虑反应活性，矿化顺序应为Ca＞Mg. 富含钙镁成分的长石、橄榄石和辉石等因其反应活性被认为是CO_2矿化最重要的矿化原料．

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