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**Article:**

Colantuono, G and Cockerill, T (2017) Selective strategy for solid sorbent replacement in CCS. *Chemical Engineering Research and Design*, 120. pp. 82-91. ISSN: 0263-8762

<https://doi.org/10.1016/j.cherd.2017.01.030>

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## Accepted Manuscript

Title: Selective strategy for solid sorbent replacement in CCS

Author: Giuseppe Colantuono Timothy Cockerill

PII: S0263-8762(17)30083-7

DOI: <http://dx.doi.org/doi:10.1016/j.cherd.2017.01.030>

Reference: CHERD 2560



To appear in:

Received date: 4-10-2016

Revised date: 25-1-2017

Accepted date: 30-1-2017

Please cite this article as: Giuseppe Colantuono, Timothy Cockerill, Selective strategy for solid sorbent replacement in CCS, *Chemical Engineering Research and Design* (2017), <http://dx.doi.org/10.1016/j.cherd.2017.01.030>

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The continuous replacement of solid sorbent in post-combustion CCS loops is modeled.

The known method removes/replaces a constant amount of sorbent after each iteration.

Known method discards fresher material, too, as the looping sorbent is fully mixed.

We can sort removed CO<sub>2</sub>-loaded sorbent: the fresher is denser due to higher capacity.

Our novel strategy puts freshest sorbent back; we compute the reduced need of sorbent.

Accepted Manuscript

# Selective strategy for solid sorbent replacement in CCS

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## Abstract

An innovative method for sorbent replacement in the looping of a generic solid sorbent for post-combustion carbon capture and sequestration (CCS) is introduced. First, the standard replacement method is revisited with some original results presented. A new strategy is then modeled, aimed at selectively replacing the material as it degrades. This method exploits the density difference, after adsorption, between relatively fresh, CO<sub>2</sub>-laden sorbent and relatively degraded material, with small residual adsorption capacity. The model is then applied to values of degradation rate within the experimental range available in scientific literature for silica-supported amines (SSA). The selective removal strategy ideally allows a saving of 37% of the sorbent with respect to the standard, undifferentiated replacement considered in first place, while keeping the same adsorptive capacity of the system.

*Keywords:* carbon capture loop; solid sorbent; silica-supported amines; capacity degradation; sorbent replacement; make-up flow.

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## 1. Introduction

Novel solid sorbents offer advantages over more established liquid amines for application in next generation carbon dioxide capture plants. In particular, their small thermal mass is expected to produce a more energy efficient capture process, while other physical and chemical properties result in a lower toxicity (Buist et al., 2015; McDonald et al., 2014). The capacity of a solid sorbent to capture carbon dioxide degrades over time with the number of sorption/desorption cycles (*cy*) endured, and hence there is an on-going need to replace material in order to maintain plant performance. With calcium looping (CaL), the input mass rate of fresh sorbent can be of the same order of magnitude as that of the fuel supply (Hanak et al., 2015); however, low sorbent cost makes replacement less of an obstacle to an economically viable process. Novel solid sorbents can

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0047 be very expensive instead, such that replacement rate has a significant impact  
0048 on operating costs.

0049 Minimizing the fresh sorbent requirement for next generation CCS plants is  
0050 therefore vital to make the technology economically viable. The only replace-  
0051 ment method considered so far (Abanades, 2002) substitutes a fixed mass of  
0052 randomly-picked sorbent particles each time a sorption/desorption looping  $cy$   
0053 takes place. While effective in maintaining plant performance, this approach  
0054 discards both degraded and recently added material from the well-mixed circu-  
0055 lating sorbent.

0056 This study investigates a modified strategy in which the sorbent is sorted  
0057 by density after removal in order to return to the loop the still-active particles,  
0058 therefore minimizing the unnecessarily replaced material. Replacement occurs  
0059 after the sorption stage, when the fresher material has a higher density thanks  
0060 to its higher affinity for carbon dioxide. In principle, this allows only materi-  
0061 al below a chosen density threshold, corresponding to a particular capacity  
0062 threshold, to be removed. A mathematical model is developed, to investigate  
0063 the key characteristics of the replacement process. Replacement rate reduction  
0064 is computed as function of key sorbent properties and number of  $cy$  undergone  
0065 by the system.

0066 The present work has been carried out in support of a program focused on  
0067 the development of a novel Silica Supported Amine (SSA) adsorbent for CO<sub>2</sub>  
0068 capture from gas-fired power plants (Liu et al., 2013). However, many kinds  
0069 of solid adsorbents are under consideration (Wang et al., 2014a; Huck et al.,  
0070 2014), based on a variety of solid substrates (Kong et al., 2015; Hao et al., 2013;  
0071 Plaza et al., 2012): the potential application of the analysis is therefore broad.

## 0072 0073 **2. Degradation and replacement rate for solid sorbents**

0074  
0075 The replacement rate depends on the sorbent rate of loss of adsorption capaci-  
0076 ty (degradation) per  $cy$ . Table 1 reports the experimental degradation rates of  
0077 several silica-supported amines (SSA). Significant dissimilarities exist between  
0078 testing a solid sorbent in the lab (e.g. Sayari et al., 2012) and conditions in a  
0079 real plant. Laboratory experiments are usually performed on few kg of sorbent  
0080 or less, while industrial loops are expected to move many thousands of kg in  
0081 a continuous process. In the lab, sorbent is often kept in the adsorption mode  
0082 until CO<sub>2</sub> saturation occurs. The batch then sometimes undergoes the desorp-  
0083 tion phase in the same location, usually at higher temperature and for a longer  
0084 time (e.g. Franchi et al., 2005). No study seems to go beyond few tens of  $cy$ ,  
0085 which is a major knowledge gap as industrial applications are likely to require  
0086 thousands of  $cy$ .

0087 When a continuous looping is reported (in Zhao et al., 2013a, sorbent is  
0088 moved back and forth from an adsorption to a desorption vessel), the number  
0089 of  $cy$  is still very small, for a total of some tens of hours: sorbent is not nearly  
0090 fully degraded. In fact, some materials reported in Table 1 do not display  
0091 any noticeable degradation: these are probably worth a deeper investigation.  
0092 Some degradation trends can be hypothesized (Fig. 1) for the more decay-prone

Table 1: The constitutive relationship between age and adsorbing capacity is reported from the experimental studies cited in first column.  $N$ , the total number of adsorption/desorption cycles, appears in third column. Most studies are in good agreement with a linear fit of negative slope  $\gamma'$  (column 4) representing the percent drop per  $cy$ :  $\gamma' = 100\gamma$ , where  $\gamma$  is the slope in the main text. A few cases show a seemingly nonlinear decay in the initial few  $cy$ , followed by an approximate linear trend; such initial nonlinearity is neglected here, as what matters is the behavior in the long run (from 10 to  $10^3 cy$ ). BTC stands for “breakthrough capacity” (Zhang et al., 2014b): the adsorption phase is considered achieved once  $CO_2$  concentration in the flue gas flowing out of the adsorption vessel falls to 10% of  $CO_2$  concentration in the input flue gas. Slopes are normalized such that the capacity of fresh sorbent ( $\beta$  in the main text) equals 1. The trends reported in this table are depicted in Fig. 1.

Reference	Sorbent name	$N$	$\gamma', \frac{\%}{cy}$	Notes
(Zhang et al., 2014b)	40% PEI-silica	24	-1.4	dry; BTC
		57	0.0	moist; BTC
(Franchi et al., 2005)	6.98DEA/PE-MCM	7	-0.6	
“ “	MCM-41-PEI50	7	-1.0	(Xu et al., 2002)
“ “	Zeolite 13X	5	0.0	regene- 350 °C
“ “		6	-7.1	rate at: 75 °C
(Zhao et al., 2013a)		10	0.0	dual fluid. beds
(Zhao et al., 2013b)	PEI600-Q10	10	-0.9	
“ “	PEI200-Q10	10	0.0	
“ “	PEI800-Q10	10	0.0	
“ “	TEPA-Q10	10	0.0	
(Sayari et al., 2012)	pMono-50/130	31	-1.6	dry
“ “	sMono-1-50/130	31	0.0	dry
“ “	Diamine-50/130	31	-1.8	dry; nonlinear
“ “	DiSamine-50/130	31	-1.8	“ “
“ “	TRI-50/130	31	-1.6	“ “
“ “	LPEI-50/130	31	-1.5	dry
“ “	LPEI-50/150	31	-2.6	dry; nonlinear
“ “	BPEI-50/130	31	-1.9	“ “
“ “	PALL-100/160	31	-0.4	“ “

materials, but can be hardly extrapolated beyond a drop in capacity of few percent.

### 3. Standard replacement method

A looping system for  $CO_2$  capture is here analyzed with regards to the gradual replacement of the solid sorbent to maintain the plant adsorption capacity. The plant (Fig. 2) moves material between two circulating fluidized beds. In the first one, the  $CO_2$ -laden flue gas is blown through the sorbent (Zhao et al., 2013a; Rodriguez et al., 2010; Wang et al., 2014c) and  $CO_2$  is adsorbed. In the second bed  $CO_2$  is removed (the sorbent is regenerated), for example by fanning nitrogen (e.g. Zhao et al., 2013a; Drage et al., 2008).

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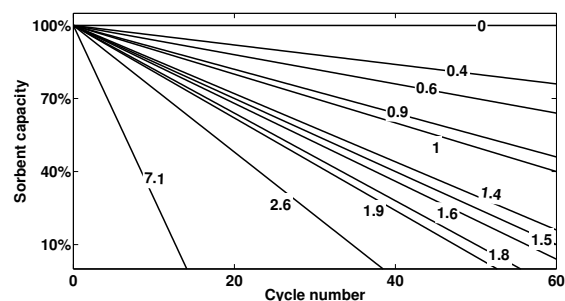


Figure 1: Decay trends from Table 1; labels indicate the slope  $|\gamma'| = 100|\gamma|$ ; the loss of adsorption capacity per  $cy$  of the aging sorbent. Capacity of fresh sorbent is set to 1.

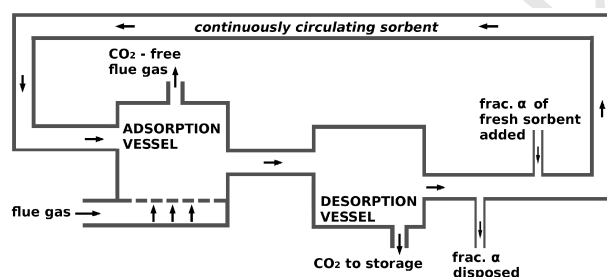


Figure 2: Schematic representation of the CCS loop with standard replacement procedure.

The system starts with a batch of fresh sorbent. After the first cycle, a fraction  $\alpha$  is removed (Fig. 2) and replaced with an equivalent amount of fresh material. Before  $cy$  2, the sorbent is therefore made up of a fraction  $(1 - \alpha)$

Table 2: Age distribution in the system after  $N$   $cy$ ;  $\alpha$  is the replacement rate. The first column tells the age of the fraction of material reported in column 2 (which sums up to 1, the entirety of material in the system); column 3 indicates the  $cy$  number at which the respective fraction was introduced in the system.

Age	Fraction of sorbent	Inserted at cycle
$k = 0$	$\alpha$	$n = N$
$k = 1$	$\alpha(1 - \alpha)$	$n = N - 1$
$k = 2$	$\alpha(1 - \alpha)^2$	$n = N - 2$
$\vdots$	$\vdots$	$\vdots$
$k = N - 1$	$\alpha(1 - \alpha)^{N-1}$	$n = 1$
$k = N$	$(1 - \alpha)^N$	$n = 0$

of 1- $cy$ -old sorbent and a fraction  $\alpha$  of fresh sorbent. After  $cy$  2, a further fraction  $\alpha$  is removed and replaced. The removed material is made up by a fraction  $\alpha(1 - \alpha)$  of 2- $cy$ -old sorbent and a fraction  $\alpha^2$  of 1- $cy$ -old sorbent.

0185 Immediately before  $cy$  3, the sorbent therefore consists of a 2- $cy$ -old fraction  
 0186  $(1 - \alpha)^2$ , a 1- $cy$ -old fraction  $\alpha(1 - \alpha)$ , and in a fraction  $\alpha$  of fresh material.  
 0187 In Table 2, the procedure is generalized to an arbitrary number of  $cy$   $N$ . Due  
 0188 to the turbulent dynamics of circulating fluidized beds (Grace et al., 2012) it is  
 0189 hypothesized that (Rodriguez et al., 2010; Grasa et al., 2009; Abanades, 2002),  
 0190 for each integer  $N > 0$ , the fresh sorbent introduced right after  $cy$   $N$  will be  
 0191 completely mixed as soon as  $cy$   $N + 1$  is complete. After  $N$   $cy$  characterized  
 0192 by a replacement rate  $\alpha$ , the amount of material of a given age  $k \leq N$  present  
 0193 in the plant is provided by the distribution of ages

$$0194 \quad f(k; \alpha, N) = \alpha^{1 - \delta_{kN}} (1 - \alpha)^k, \quad (1)$$

0196 where

$$0197 \quad \delta_{kN} = \begin{cases} 1, & \text{if } k = N \\ 0, & \text{otherwise,} \end{cases}$$

0199 is the Kronecker Delta.

0200 The average age of the circulating material is calculated by means of intro-  
 0201 ducing the weighted distribution of ages

$$0202 \quad w(k; \alpha, N) = k \alpha^{1 - \delta_{kN}} (1 - \alpha)^k \quad (2)$$

0203 and then summing from 0 to  $N$ :

$$0204 \quad \bar{K}(\alpha, N) \equiv \sum_{k=0}^N w(k; \alpha, N) = (1 - \alpha) \frac{1 - (1 - \alpha)^N}{\alpha}. \quad (3)$$

0205 Equation (3) immediately follows from Eq. (2) and the formula for the partial  
 0206 sum of the geometric series (Gradshteyn and Ryzhik, 1980). When the number  
 0207 of  $cy$   $N$  approaches infinity, the average age becomes

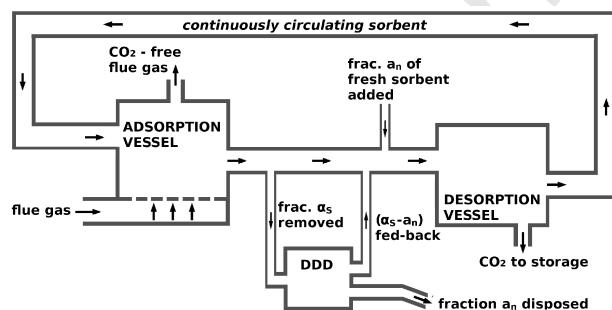
$$0208 \quad \bar{K}^\infty(\alpha) \equiv \sum_{k=0}^{\infty} w(k; \alpha, \infty) = \frac{(1 - \alpha)}{\alpha} \underset{\alpha \ll 1}{\sim} \frac{1}{\alpha}. \quad (4)$$

0209 That is, after a large number of cycles and for a small replacement rate  $\alpha$ ,  
 0210 the average age of the sorbent in the system is inversely proportional to  $\alpha$ .  
 0211 Abanades (2002) carries out a similar analysis (later expanded by Grasa et al.  
 0212 2009, Rodriguez et al. 2010 and Martínez et al. 2012) for a carbonation-calcination  
 0213 loop and computes the asymptotic value of absorption capacity for an infinite  
 0214 number of  $cy$ . Instead, average age is here computed for any finite  $N$ ; the  
 0215 asymptotic behavior is then obtained. Capacity is introduced at a later stage,  
 0216 as its dependency on age (constitutive relationship) is material dependent.

#### 0217 4. Selective replacement method

0218 Replaced sorbent  $\alpha$  for the standard method consists of perfectly mixed  
 0219 ages/capacities, as occurs for the whole system: fresher sorbent is therefore  
 0220 disposed of at the same rate of older material, which is wasteful.

0231 The difference in the mass of sorbent particles before and after adsorption  
 0232 reaches  $\sim 14\%$  in some studies (Wang et al., 2014b). According to accepted  
 0233 theories on physical adsorption (Brunauer-Emmett-Teller, or BET, and its pre-  
 0234 cursors and evolutions, see for example Rouquerol et al. 2013), the adsorbed  
 0235 gas gets confined, by the Lennard-Jones potential (Mortimer, 2000), in layers  
 0236 within few Å of the surfaces of the sorbent particles. Numerical simulations in  
 0237 Razmus and Hall (1991) show that the adsorbate's density markedly peaks in  
 0238 the adsorption layers with respect to the surrounding fluid phase; the contribu-  
 0239 tion of those layers to the volume of the porous particles is negligible, which holds  
 0240 even more for chemisorption, in which case the adsorbate is confined within a  
 0241 single layer (Dąbrowski, 2001). That is, the mass increment of particles due to  
 0242 adsorption can be regarded as a density increase only, at least at the pressure  
 0243 (within one order of magnitude of 1 bar) at which  $\text{CO}_2$  adsorption takes place  
 0244 (Murata et al., 2002).



0256 Figure 3: Scheme of the CCS loop proposed for the selective replacement procedure. The  
 0257 density discriminating device (*DDD*) is the novelty with respect to Fig. 2. Replacement  
 0258 is here posited to occur when the sorbent is loaded with  $\text{CO}_2$ , as the mass gained during  
 0259 adsorption allows to discriminate between fresh and degraded material.

0260 Gas-solid fluidized beds are of interest as potential *DDD*'s; it is proposed to  
 0261 use the  $\text{CO}_2$ -laden flue gas as the fluidizing medium, in order not to accidently  
 0262 remove from the sorbent the  $\text{CO}_2$  load, and the density difference with it.  
 0263 Denser material will then be reinserted into the looping system, upstream of  
 0264 the desorption vessel, ready for the desorption stage (Fig. 3). In order not to  
 0265 disperse  $\text{CO}_2$  in the atmosphere an extra stage is introduced, where the removed  
 0266 degraded material is regenerated prior to its disposal.

#### 0267 4.1. Possible ways to achieve density separation

0268 Density/gravity dry separation methods are subject to intense R&D efforts,  
 0269 driven by the need for burning cleaner coal to reduce pollution (e.g. Xia et al.,  
 0270 2015) and to advance mineral processing, waste recycling and other industries.  
 0271 Additional techniques are combined with fluidization to improve separation.  
 0272 Air dense medium fluidized beds (ADMFBs, Mohanta et al. 2013) have existed for  
 0273 almost a century (Fraser and Yancey, 1925). They work by mixing a "separation  
 0274 medium" (usually a finer powder than the one being sorted) with air to obtain  
 0275  
 0276

0277 the fluidizing medium, the density of which is tuned to the wanted separation  
 0278 density. Separation is ideally achieved relying on buoyancy only, like in a liq-  
 0279 uid. Turbulence due to bubble formation induces vertical mixing, thus working  
 0280 against density stratification and separation (Mohanta et al., 2013). Vibration  
 0281 is often applied to ADMFBs to reduce bubble size and mixing (Luo et al., 2003);  
 0282 stabilization can be intensified also by using a magnetizable separation medium  
 0283 and applying a magnetic field (Luo et al., 2002).

0284 Many studies report separation of particles with diameter down to half mil-  
 0285 limeter (see references in Mohanta et al., 2013, who also point out the current  
 0286 drawbacks of the method and the need of further development). Luo et al.  
 0287 (2002) employ magnetic pearls and achieve segregation of coal particles be-  
 0288 tween 0.5 mm and 6 mm, the separation density being  $\rho_0 = 1520 \text{ kg m}^{-3}$ , with  
 0289 an Ecart probable error

$$0290 \quad E_p \equiv (\rho_{75} - \rho_{25})/2 = 65 \text{ kg m}^{-3} \quad (5)$$

0291  
 0292 (values  $\rho_{25} < \rho_0 < \rho_{75}$  are defined such that the denser fraction after separation  
 0293 “erroneously” contains 25% of  $\rho_{25}$ -dense sorbent and “only” 75% of the  
 0294 denser-than-threshold material  $\rho_{75}$ . Particles with density within/outside the  
 0295  $[\rho_{25}, \rho_{75}]$  interval are harder/easier to separate, Richard et al. 2011).

0296  
 0297 Chung et al. (2006) focus on the submillimeter range (0.4 to 1.0 mm) and  
 0298 attain separation with  $E_p = 100 \text{ kg m}^{-3}$  using an ADMFB. Tenths of mm is also  
 0299 the typical size of SSA particles for carbon capture reported in some character-  
 0300 ization studies reviewed in Table 1 (e.g. Zhang et al., 2014b). Sahan and Kozanoglu  
 0301 (1997) employ a magnetized ADMFB to separate fines down to few tens of  $\mu\text{m}$ ,  
 0302 grouping particles by size prior to the separation process (e.g., 45 to 75  $\mu\text{m}$ ):  
 0303 this way, drag forces (acting on particles in proportion to their size) are compa-  
 0304 rable, and affect less the buoyancy discriminating effect.  $E_p$  is not reported, but  
 0305 their work is relevant as SSA particles for CCS can be manufactured to display  
 0306 a narrow size distribution (Zhao et al., 2013a) which helps density sorting.

#### 0307 4.2. Consequence of separation errors

0308  
 0309 The density range  $2E_p$  (Eq. 5) for the just reported studies is comparable  
 0310 to the  $\sim 200 \text{ kg/m}^3$  estimated difference between fresh- and worn-out- post-  
 0311 adsorption SSA (based on the adsorption capacity of 142 mg of  $\text{CO}_2$  per g of  
 0312 sorbent, reported by Wang et al. 2014b, multiplied by the  $1400 \text{ kg/m}^3$  SSA  
 0313 density of Zhang et al. 2014a). Some degree of separation could already be  
 0314 possible, at least between freshest and oldest SSA particles; development of  
 0315 sorbents with higher adsorption capacity will increase density difference between  
 0316 fresh and spent sorbent, making separation sharper.

0317  
 0318 Aside from the separation technique it is necessary to estimate the outcome  
 0319 of mistakenly categorizing a particle of density  $\rho_0 - \epsilon\rho_0$  as having density  $\rho_0 +$   
 0320  $\epsilon\rho_0$  (with  $\epsilon < 1$ ) while, on the other side, labeling a  $\rho_0 + \epsilon\rho_0$  particle as a  
 0321  $\rho_0 - \epsilon\rho_0$  one. If  $\epsilon \ll 1$ , the DDD gets rid of a particle of capacity slightly higher  
 0322 than the retained particle. Highly probable small errors have therefore small  
 impact. The errors with notable effects (e.g. exchanging a particle with 80%

0323 capacity with one of 20%) are the least probable instead. Such an advantageous  
 0324 inverse relationship between sorting errors magnitude and the likelihood of their  
 0325 occurrence is not found in the cited studies about density separation devices.  
 0326 Density sorting is there employed as a binary classifier, to filter out impurities  
 0327 in coal or other materials. A separation error in those contexts has always the  
 0328 maximal outcome: retaining the wrong species in place of the desired one, no  
 0329 matter how small the density difference is. Viceversa, the process outlined here  
 0330 will be practically unaffected by separation errors at small density differences,  
 0331 and may still be worthwhile in presence of large separation errors.

0332 As a simple measure of the effectiveness of a coarse separation, a set of 101  
 0333 pairs of CO<sub>2</sub>-loaded particles is considered; each pair is labeled from 0 to 100 to  
 0334 indicate age  $n$ . A density-separation process is then performed, with the aim  
 0335 of obtaining two sets of 101 particles each. In case of perfect separation, set A  
 0336 contains the older/lighter particles (50 pairs from age 51 to age 100, plus one  
 0337 particle of age 50), whilst set B contains the fresher/denser particles (50 particle  
 0338 pairs from age 0 to age 49, plus one particle of age 50); the sum of ages is 7550 for  
 0339 set A and 2550 for set B. In case of separation able to discriminate only particles  
 0340 with  $n \geq 90$  from particles with  $n \leq 10$  (i.e. density difference  $160 \text{ kg m}^{-3}$  or  
 0341 larger, being  $200 \text{ kg m}^{-3}$  the difference between fresh and completely worn-out  
 0342 sorbent estimated few lines above), the age sum is 6040 for set A and 4060 for  
 0343 set B, meaning that 40% of the adsorption capacity imbalance in the system  
 0344 can be discriminated. In case of a  $120 \text{ kg m}^{-3}$  *DDD*'s resolution limit (i.e., the  
 0345 *DDD* is able to discriminate only particles with  $n \geq 80$  from particles with  
 0346  $n \leq 20$ ), 70% of sorption capacity difference can be separated. This simple  
 0347 estimate shows how the *DDD* can be far from ideal but still useful.

0348 Fines may form in the capture plant due to particles crumbling; this occurs  
 0349 almost only in the first few cycles. On the other hand, smaller particles tend to  
 0350 agglomerate as *cy* number increases (Fig. 3 in [Zhang et al., 2014b](#)). This reduces  
 0351 the spread of the particles' size distribution, therefore helping the sharpness of  
 0352 *DDD* separation.

## 0354 5. Mathematical model of the selective replacement

0355 The amount of make-up sorbent needed in a loop with a *DDD* is determined  
 0356 and compared with the larger quantity needed in the standard case. The *DDD*  
 0357 operates with a density threshold reached by the progressively degraded CO<sub>2</sub>  
 0358 -loaded sorbent after  $M$  *cy*. During the initial  $M-1$  *cy*, no material is removed.  
 0359 Right after *cy*  $M$ , a predetermined fraction  $\alpha_S$  is taken away and replaced with  
 0360 fresh sorbent (age 0). After *cy*  $M+1$  a further fraction  $\alpha_S$  is removed; this  
 0361 amount is not homogeneous, because the plant contains the fraction  $(1 - \alpha_S)$   
 0362 of original sorbent (now aged  $M + 1$ ), plus the fraction  $\alpha_S$  of sorbent inserted  
 0363 at the end of the previous *cy*. We adopt the "ket" notation  $| \rangle$  to indicate the  
 0364 *cy* number at which the sorbent was inserted as fresh, and therefore label with  
 0365  $|M\rangle$  the material inserted right after *cy*  $M$ . The expression  $(1 - \alpha_S) |0\rangle$  denotes  
 0366 the amount of the oldest material that is still present in the system right after  
 0367 *cy*  $M$  and the following replacement procedure has been accomplished. As  
 0368

0369 a consequence, the fraction  $\alpha_S$  removed after  $cy\ M+1$  has two components:  
 0370  $\alpha_S(1 - \alpha_S) |0\rangle$  and  $\alpha_S^2 |M\rangle$ . The hypothesis that all the ages in the plant are  
 0371 completely mixed holds also for selective replacement.

0372 The *DDD* outlined above now starts to operate: the component  $\alpha_S^2 |M\rangle$  can  
 0373 be separated from the older, lighter component  $\alpha_S(1 - \alpha_S) |0\rangle$ , and returned to  
 0374 the looping system. The net effect of the replacement procedure is to substitute  
 0375  $\alpha_S(1 - \alpha_S) |0\rangle$  with  $\alpha_S(1 - \alpha_S) |M+1\rangle$ . The composition of the sorbent ready  
 0376 for  $cy\ M+2$  is therefore  $(1 - \alpha_S)^2 |0\rangle + \alpha_S |M\rangle + \alpha_S(1 - \alpha_S) |M+1\rangle$ .

0377 The fraction removed after  $cy\ M+2$  is then  $\alpha_S \cdot [(1 - \alpha_S)^2 |0\rangle + \alpha_S |M\rangle +$   
 0378  $\alpha_S(1 - \alpha_S) |M+1\rangle]$ ; the last two terms are fed-back into the desorption vessel,  
 0379 implying that the truly disposed-of material is only  $\alpha_S(1 - \alpha_S)^2 |0\rangle$ , replaced by  
 0380  $\alpha_S(1 - \alpha_S)^2 |M+2\rangle$ . The difference with the standard procedure ([Abanades,](#)  
 0381 [2002](#)) resides in putting back into the system the sorbent that is less than  $M$   
 0382  $cy$  old.

0383 In order to derive a general expression for the replacement, the following  
 0384 procedure is formulated for an arbitrary number of  $cy\ N$ , with  $M$  denoting the  
 0385 age threshold (the number of  $cy$  needed to degrade the material). The sorbent  
 0386 in the system is divided in three categories: the fraction of material present from  
 0387 the outset, labeled by  $|0\rangle$ ; the fractions introduced after  $cy\ M$  and before  $N-M$ ,  
 0388 labeled by  $|M\rangle, |M+1\rangle, |M+2\rangle, \dots, |N-M\rangle$ ; and the fractions of sorbent less  
 0389 than  $M-cy$  old, labeled by the highest  $cy$  numbers, from  $|N-M+1\rangle$  to  $|N\rangle$ .  
 0390 The material designated by the highest labels is the one that the *DDD* puts  
 0391 back into the desorption vessel, as schematized in Fig. 3. The age distribution  
 0392 of the sorbent, after the replacement occurring between  $cy\ N$  and  $N+1$ , is

$$0393 |S_{N,M}\rangle = |0\rangle, \quad \text{if } N < M \quad (6)$$

$$0394 |S_{N,M}\rangle = (1 - \alpha_S)^{N-M+1} |0\rangle + \sum_{n=M}^{N-M} a_n (1 - \alpha_S)^{N-M-n+1} |n\rangle +$$

$$0395 + \sum_{n=N-M+1}^N H(n - M + 1) a_n |n\rangle, \quad \text{if } N \geq M; \quad (7)$$

0401 the summations (for Eq. 7 and all the following ones) are nil if the upper limit  
 0402 is smaller than the lower one. The quantity

$$0403 H(X) = \begin{cases} 1, & \text{if } X > 0; \\ 0, & \text{otherwise} \end{cases} \quad (8)$$

0404 is the Heaviside step function according to the  $H(0)=0$  convention, while the  
 0405 coefficients  $0 \leq a_n \leq 1$  in Eq. (7) are unknown and need to be determined. The  
 0406  $a_n$ 's represent the replacement rate at  $cy\ n$ , as shown in Fig. 4: the fraction  
 0407  $\alpha_S$  is picked and processed by the *DDD*; the fraction  $a_n$  (the "oldest" subset  
 0408 of  $\alpha_S$ ) is replaced with fresh sorbent, and the fraction  $\alpha_S - a_n$  is put back  
 0409 in the system.  $a_n$  varies with the  $cy$  number, but gradually approaches its  
 0410 asymptotic value  $a_\infty$ . The norm (a.k.a. the modulus for ordinary vectors) of  
 0411  
 0412  
 0413  
 0414

0415  $|S_{N,M}\rangle$  (Eq. 7) is equal to 1, as  $|S_{N,M}\rangle$  is the sum of all the components in the  
0416 system.

0417 The case  $N < M$  (Eq. 6) can be neglected, as it corresponds to ending the  
0418 loop before the threshold age is reached. By multiplying each  $|n\rangle$  by the age  
0419  $k = N - n$  in Eq. (7), the sorbent average age is computed, in analogy with  
0420 Eq. (3):

$$\begin{aligned} 0421 \bar{K}_S &= N(1 - \alpha_S)^{N-M+1} + \sum_{n=M}^{N-M} a_n (N - n) (1 - \alpha_S)^{N-M-n+1} + \\ 0422 &+ \sum_{n=N-M+1}^N H(n - M + 1) (N - n) a_n. \end{aligned} \quad (9)$$

0423 Starting from Eq. (7) we now define

$$\begin{aligned} 0424 |S_{N,M}^M\rangle &= |S_{N,M}\rangle - \sum_{n=N-M+1}^N H(n - M + 1) a_n |n\rangle \equiv \\ 0425 &\equiv (1 - \alpha_S)^{N-M+1} |0\rangle + \sum_{n=M}^{N-M} a_n (1 - \alpha_S)^{N-M-n+1} |n\rangle, \end{aligned} \quad (10)$$

0426 the portion of sorbent in the system that has already crossed the threshold  $M$ ,  
0427 and from which the removed sorbent must be drawn. The amount of materi-  
0428 al replaced by fresh matter after each *cy*  $l = 0, 1, 2, \dots, N - 1$  is therefore the  
0429 following fraction of  $|S_{l,M}^M\rangle$ :

$$0430 a_0 = 1 \quad (11)$$

$$0431 a_1 = a_2 = \dots = a_{M-2} = a_{M-1} = 0 \quad (12)$$

$$0432 a_M = \alpha_S a_0 \equiv \alpha_S \quad (13)$$

0433  $\vdots$

$$\begin{aligned} 0434 a_{l+1} &= \alpha_S \|S_{l,M}^M\| \equiv \\ 0435 &\equiv \alpha_S \left[ a_0 (1 - \alpha_S)^{l-M+1} + \sum_{n=M}^{l-M+1} a_n (1 - \alpha_S)^{l-M-n+1} \right]. \end{aligned} \quad (14)$$

0436 The material  $a_{l+1} |l+1\rangle$ , inserted right after *cy*  $l+1$ , starts to be removed after  
0437 *cy*  $l+M+1$ . The quantity of sorbent labeled by  $|l+1\rangle$ , which is still present  
0438 in the system right after *cy*  $l+M+p \leq N$ , amounts to  $a_{l+1}(1 - \alpha_S)^p$ ;  $p$  is a  
0439 positive integer.

0440 The  $\{a_n\}$  sequence represents the actual replacement rate of the selective  
0441 method (Fig. 4-A, dashed curve), and varies with the *cy* number  $n$ . The differ-  
0442 ence between the “nominal”, constant replacement rate  $\alpha_S$ , and the actual rate,  
0443  $a_n$ , represents the sorbent above the density threshold, which is returned into  
0444 the system just before *cy*  $n+1$ .

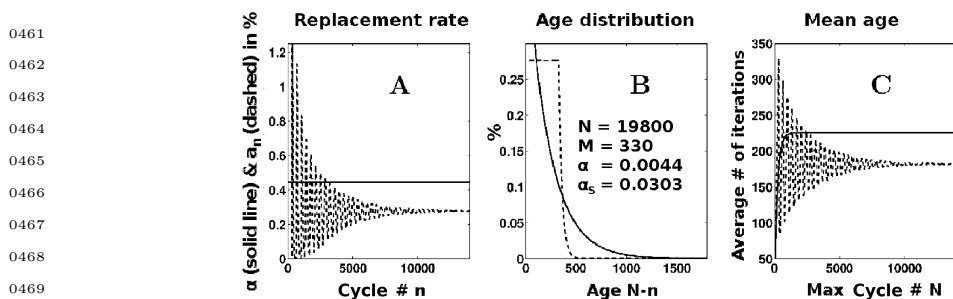


Figure 4: Panel A: the standard procedure for sorbent replacement (constant rate  $\alpha \approx 0.44\%$ ) is compared to the selective strategy (dashed line; nominal replacement rate  $\alpha_S \approx 3.03\%$ , corresponding to the out-of-box maximum of the curve at  $n = M$ ). The total number of  $cy$  is  $N$ , while  $M$  indicates the age threshold for the selective case; that is, the number of  $cy$  after which the sorbent can be disposed of. Age is proportional to sorbent's capacity (Table 1); hence, to the density of the  $\text{CO}_2$ -loaded particles. The difference between the asymptotic value  $a_\infty \approx 0.28\%$  of the selective method and the standard method's  $\alpha \approx 0.44\%$  implies that 37% of sorbent can be saved by the selective procedure. Panel B shows the distribution of ages in the system. Panel C reports the average age of the sorbent in the system as function of the number of elapsed  $cy$ . The parameters shown in Panel B are common to all the three plots. The  $\alpha$  and  $\alpha_S$  rates have been chosen to be in a proportion such that the ensuing age distribution in the system leads to the same asymptotic capacity in both cases (Fig. 5A).

Equations (11-14) define the sought recursive formula:  $a_{l+1}$ , the amount of material to be replaced after  $cy$   $l+1$ , is a linear combination of  $|0\rangle$  and of the preceding replacements  $|M\rangle, \dots, |l-M\rangle$ : that is, all and only the labels older than  $M$   $cy$ . Equation (11) holds because  $|0\rangle$  is the label of the sorbent that completely fills the system up before  $cy$  1. Equations (12) reflect the fact that, before the initial load of sorbent reaches the threshold age  $M$ , no replacement occurs. The first replacement occurs right after  $cy$   $M$ , when a fraction  $\alpha_S$  is removed (Eq. 13). As time and cycle number advance, as soon as any sorbent label  $|n\rangle$  becomes  $M$   $cy$  old, it starts to be depleted by a factor  $(1 - \alpha_S)$  per  $cy$ . E.g., right after  $cy$  200, only  $\sim 21\%$  of the fraction inserted at  $cy$  100,  $a_{100}$ , is present in the system, as  $(1 - \alpha_S)^{200 - M - 100 + 1} \equiv (1 - \alpha_S)^{51} = 0.212$ , for  $M = 50$  and  $\alpha_S = 3\%$ .

## 6. Constitutive relationship between capacity and age

Adsorption capacity can be related to the number of endured adsorption/desorption cycles ("age") using the experimental results cited in Table 1; in most cases, capacity (column 4) fits a linearly decreasing trend with respect to  $cy$  number. A significant exception is LPEI-50/150 in Sayari et al. (2012), which resembles a negative exponential. Such a shape may be realistic for other materials as well: as soon as tests will last enough to bring capacity closer to zero, a horizontal asymptotic may be expected. Here, decreasing linear trends are adopted (Fig. 1); capacity is then set to zero for every  $cy$  number greater than the abscissa intercept, in order to avoid non-physical negative values; this choice

0507 makes the constitutive relationship piecewise linear:

$$0508 \quad C(k) = (\gamma k + \beta) \cdot H(\gamma k + \beta), \quad \gamma \leq 0, \quad \beta \geq 0; \quad (15)$$

0510 the ordinate intercept  $\beta$  is the capacity of fresh sorbent, set to 1 in the numerical  
0511 experiments (Figs. 4-6) and in Fig 1.

### 0513 6.1. System's adsorption capacity with standard replacement

0514 The distribution of ages in the system is known (Eq. 1); recalling that Eq. (2)  
0515 was obtained by weighting the age distribution by the age itself, we now use as  
0516 weight the capacity  $C(k)$  introduced in Eq. (15). The distribution of capacities  
0517 in the system will then be  
0518

$$0519 \quad c(k; \alpha, N) = (\gamma k + \beta) \cdot H(\gamma k + \beta) \alpha^{1-\delta k N} (1 - \alpha)^k. \quad (16)$$

0521 Consequently, the average capacity is

$$0522 \quad \bar{C}(\alpha, N) = \sum_{k=0}^N (\gamma k + \beta) \cdot H(\gamma k + \beta) \alpha^{1-\delta k N} (1 - \alpha)^k. \quad (17)$$

### 0526 6.2. System's adsorption capacity with selective replacement

0527 In the selective case, too, the average capacity can be expressed starting  
0528 from average age (Eq. 9) with capacity  $C(k)$  (Eq. 15) playing the role of the  
0529 weighting function in lieu of age  $k \equiv N - n$ :  
0530

$$0531 \quad \bar{C}_S = C(N) (1 - \alpha_S)^{N-M+1} + \sum_{n=M}^{N-M} a_n C(N - n) (1 - \alpha_S)^{N-M-n+1} +$$

$$0532 \quad + \sum_{n=N-M+1}^N H(n - M + 1) C(N - n) a_n. \quad (18)$$

0533 Average capacity  $\bar{C}_S$  therefore relies on the recursion formulas for the actual  
0534 replacement rate  $a_n$  (Eqs. 11-14), which are determined numerically (Figs. 5,  
0535 6D).  
0536  
0537

## 0542 7. How do the two replacement strategies compare?

0543 To compare the sorbent requirement of the selective method against the  
0544 standard one, we ask for the asymptotic value of the average capacity for large  
0545  $N$  to be the same in both cases (Fig. 5A). This is accomplished by fixing the  
0546 nominal replacement rate  $\alpha_S$  of the selective case (dashed line) to  $\sim 6.87$  times  
0547 the standard replacement rate  $\alpha$  (Fig. 4A), and leads (Fig. 4C) to a lower average  
0548 age with respect to the standard system (solid line), as the older-than-threshold  
0549 sorbent is selectively, more effectively removed. Such a lower average age does  
0550 not translate into higher capacity however, because old-enough sorbent has zero  
0551 capacity regardless of age.  
0552

0553 The ratio  $\alpha_S/\alpha$  causing the asymptotic matching is controlled by the decay  
 0554 rate  $\gamma$ , as shown in Fig. 5: with  $\gamma$  as in Fig. 5A, the asymptotic value of the  
 0555 selective replacement case (dashed line) is equal to the standard case (solid line).  
 0556 Keeping  $\alpha_S$  and  $\alpha$  unchanged for a more resilient sorbent (Fig. 5B-C, smaller  
 0557  $|\gamma|$ ) causes the asymptotic mismatch instead. Even more important, unwanted  
 0558 replacement and disposal of still-fresh sorbent occur both in the standard and  
 0559 selective case, as shown by the higher capacity of the system ( $\sim 0.8-0.9$  vs  $0.5$ ).  
 0560 In order to keep the average capacity constant while increasing resilience (that  
 0561 is, while decreasing  $|\gamma|$ )  $\alpha_S$  and  $\alpha$  need to be reduced accordingly, as shown in  
 0562 Fig. 6.

0563 Having set the replacement rates  $\alpha$  and  $\alpha_S$  as in Fig. 4, Fig. 5 displays  
 0564 the ensuing behavior of capacity as function of the degradation rate  $\gamma$ , which  
 0565 has been fixed to a range of values inversely proportional to the threshold  $M$ :  
 0566  $-0.9/M$ ,  $-0.3/M$ , and  $-0.09/M$ . In Fig. 5A (and Fig. 6D), the standard decay  
 0567 rate coincides with the asymptotic value of the selective replacement's capacity,  
 0568 that oscillates around the mean value with the oscillations amplitude decreasing  
 0569 as progressive  $cy$  number increases.

0570 In a real power plant the initial capacity oscillations need to be damped, in  
 0571 order to suppress/smooth out the few first, very low relative minima (indicating  
 0572 insufficient capture). This could be accomplished for example by starting with  
 0573 a prescribed distribution of ages rather than with a batch of fresh sorbent.  
 0574 Starting capture operations with a distribution of ages approximating the one  
 0575 shown in Fig. 4B for  $N = 19800$  (dashed curve, selective procedure) places the  
 0576 system in an operational mode close to the capacity asymptote  $\bar{C}_S = 0.5$  shown  
 0577 in Fig. 5A. Approximating initially such a distribution would be relatively easy,  
 0578 as all the ages above  $1/|\gamma| \approx 370$   $cy$  are equivalent for the sake of both  $\text{CO}_2$   
 0579 capacity (nil) and density separation.

0580 The parameters  $M$ ,  $\alpha_S$ , and  $\gamma$  in Figs. 5A and 6D have been selected in  
 0581 order to exploit the sorbent at least down to 10% of its fresh capacity. Below  
 0582 this threshold value, the sorbent becomes disposable. This does not mean it will  
 0583 be disposed of immediately after crossing the threshold, as the  $DDD$ , each time,  
 0584 processes a randomly-picked fraction of the circulating sorbent. Figs. 5B-5C  
 0585 summarize the (impractical) configuration in which the chosen threshold  $M$   
 0586 and the replacement rates  $\alpha$  and  $\alpha_S$  make a more (with respect to Fig. 5A)  
 0587 resilient sorbent disposable at  $\sim 80-95\%$  of full capacity.  $M$ ,  $\alpha$ , and  $\alpha_S$  should  
 0588 be modified accordingly in order to compensate for the reduced  $|\gamma|$  to obtain  
 0589 a situation similar to Fig. 5A, with an average capacity around 50%, an al-  
 0590 most complete exploitation of the sorbent and a consequent detectable density  
 0591 difference between fresh and disposable sorbent: this is attained in Fig. 6D.

0592 On the other hand, increasing the threshold in Fig. 5A to  $M = -1/\gamma = 370$   
 0593 in order to exploit capacity entirely would require  $\sim 50\%$  more sorbent being  
 0594 processed by the  $DDD$ , consequently making the  $DDD$  larger and costlier. The  
 0595 choice of the parameters is therefore intertwined with the economic equilib-  
 0596 rium between the plant components, the sorbent cost and the  $DDD$  separation  
 0597 effectiveness, and will be addressed in an ongoing study on techno-economics  
 0598 (e.g. Hurst et al., 2012; Odeh and Cockerill, 2008a,b) and uncertainty analysis

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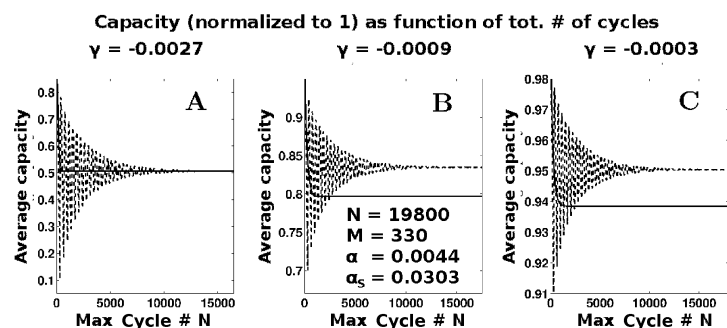


Figure 5: Normalized capacity (ratio of average capacity to the capacity of fresh sorbent) as function of the total number of  $cy$   $N$ , for both the standard case (after Eq. 17 with  $\beta = 1$ ; solid line) and the selective procedure (Eq. 18; dashed line). Three values for the constitutive relation's slope are considered here, falling within the range of the  $\gamma$  values displayed in Table 1 (spanning from  $\sim -0.07$  to  $\sim 0$ ; the latter value corresponds to undetectable degradation in the small number of reported cycles). The value of the degradation rate  $\gamma$  of Panel A is divided by 3 in Panel B and by 10 in Panel C. The normalized average capacity values  $\bar{C}$ ,  $\bar{C}_S$  shown in these plots correspond to the average age values  $\bar{K}$ ,  $\bar{K}_S$  displayed in Fig. 4C. The parameters shown in Panel B are common to all the three plots and to Fig. 4.

of SSA-based  $\text{CO}_2$  capture.

Figure 6A-C represent the evolution of Fig. 4A-C, respectively, for a tenfold increase of the threshold  $M$ , the according tenfold growth of the number of total  $cy$   $N$ , and a tenfold reduction of the  $\alpha$ ,  $\alpha_S$ , and  $a_n$  rates. Such combined parameters' change has the effect of rescaling the axes while keeping Fig. 6A-C perfectly similar to Fig. 4A-C. Figure 6D, the evolution of Fig. 5A, shows that capacity is left unaltered if the above change in parameters' values is combined with a tenfold reduction of  $|\gamma|$ . The magnitude of the make-up flow of fresh sorbent therefore critically depends on sorbent's resilience, quantified by the slope  $\gamma$  in the hypothesis of a linear age-capacity constitutive relationship.

Selective actual replacement rate (Fig. 4A, dashed line) and average age (Fig. 4C) settle reasonably close to their asymptotic values after a number of  $cy$  less than  $10M$  (which is the value of  $N$  used in the numerical computations summarized in Figs. 4, 5 and 6). The age distribution, too (Fig. 4B), is insensitive to increasing  $N$  beyond  $\sim 10M$ : the sorbent labels (ages) present in the system in significant amounts are the ones inserted in the most recent cycles, regardless to the overall length of the process.

Mathematically proving the convergence of the series defined by Eqs. (11-14) is not the aim of the present work. To ensure convergence for any practical purpose, a simulation has been run with the same parameters specified in Fig. 4:  $\alpha = 3 \cdot 10^{-3}$ ,  $\alpha_S = 4.2 \cdot 10^{-3}$ ,  $M = 330$ , but the total number of  $cy$  increased to  $N = 3.3 \cdot 10^5$ . With a single complete  $cy$  taking  $\sim 2$  hr, as reported for example by Zhang et al. (2014b), the corresponding time span is  $\sim 75$  years. The empirical asymptotic value  $a_\infty \approx 2.8 \cdot 10^{-3}$  for the selective case (Fig. 4A) is confirmed also on this timescale, with fluctuations around the true value in the order of  $10^{-15}$ .

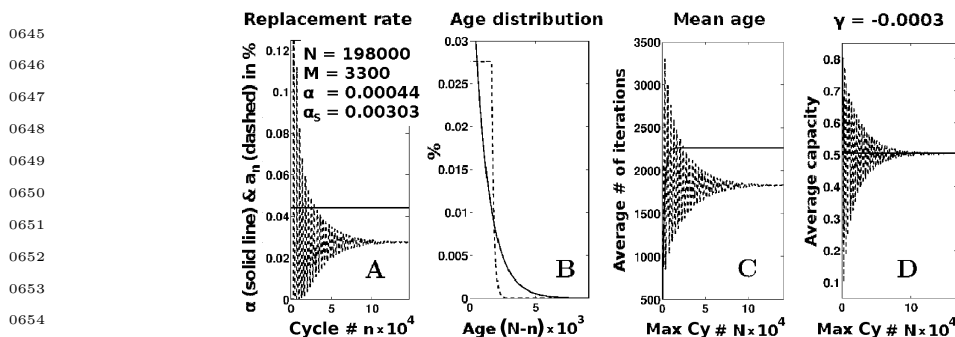


Figure 6: Panels A-C are like Fig. 4A-C but with a tenfold increase of threshold  $M$  and number of total  $cy$   $N$ , and a tenfold decrease of  $\alpha$ ,  $\alpha_s$ , and  $a_n$ ; the parameters shown in Panel A are common to all the four plots. Panel D is similar to Fig. 5A: normalized capacity remains unaltered if, besides the above parameters' changes,  $|\gamma|$  is reduced by a factor 10.

The selective replacement strategy simulated as reported in Fig 4, Fig 5A, and Fig 6 allows to save ideally  $\sim 37\%$  of sorbent with respect to the standard strategy. A real *DDD* will have this figure modulated by separation efficiency, a simple “worst-case” estimate of which has been provided at the bottom of Section 4.1.

## 8. Conclusions and recommendations

A key challenge for many types of post-combustion CCS plants is to maintain the effectiveness of the carbon-dioxide capturing sorbent as the plant operates over the long term. With the current interest in solid sorbents, identifying strategies to maintain plant performance is an important topic, that has not been thoroughly covered in the literature.

Most work to date has investigated schemes whereby a constant fraction of the sorbent material is replaced from the plant each time it iterates through the absorption/desorption cycles. As the sorbent particles are well mixed, this approach has the disadvantage that both recently added, relatively-fresh particles will be replaced as well as much older, degraded material.

Building on the work of Abanades (2002), we have analyzed the continuous partial replacement of solid sorbent in a post-combustion CCS adsorption/desorption loop. Analytical expressions have been developed for the distribution of the sorbent particles age and the corresponding adsorption capacity as a function of the number of adsorption/desorption cycles carried out. This analysis allows the potential benefits of a novel strategy for sorbent replacement, exploiting the decrease of adsorption capacity with sorbent age, to be thoroughly modeled and evaluated.

The novel strategy is initially similar to the previously analyzed standard replacement method: a constant fraction of sorbent is removed from the plant with each cycle of the absorption/desorption loop. The innovation proposed here is that the removed particles are subsequently sorted by density. The

0691 reduced capture capacity of the older particles means that, after the adsorption  
0692 stage, they will have a lower density than the fresher material. As it has been  
0693 demonstrated that the adsorption process has no impact on particle volume,  
0694 grading by density is therefore equivalent to grading by capture capacity, and  
0695 hence particle age. The older fraction of the separated sorbent can then be  
0696 replaced with fresh material, and the newer fraction returned to the plant,  
0697 thereby minimizing the need for new sorbent.

0698 Results indicate that, under optimal separation, there would be a 37% make-  
0699 up flow reduction compared to the strategy without density separation. This  
0700 figure depends on the separation efficiency. Whether the *DDD* approach is  
0701 worthwhile depends in principle also on the sorbent's cost and degradation rate  
0702  $\gamma$ , as well as on the expenditure on the separation apparatus. The cost the  
0703 *DDD* adds to generated power scales with the *DDD* size and therefore with the  
0704 amount of material per *cy* in need of density sorting, which is proportional to  $\gamma$ .  
0705 The techno-economics of selective replacement will be the subject of a follow-  
0706 up paper. For a relevant portion of pairs of sorbent's cost and degradation  
0707 rate values, initial analysis indicates that the *DDD* outlay is much smaller than  
0708 the expense on material the *DDD* prevents; the overall savings are therefore  
0709 significant.

0710 The device to accomplish density separation could be an adaptation/evolu-  
0711 tion of Air Dense Medium Fluidized Beds. ADMFBs use fines in addition to air  
0712 as the fluidizing medium, which is therefore characterized by a tunable density,  
0713 to be fixed to the separation threshold: this allows buoyancy-driven separation  
0714 like in liquids. Separation can be aided by vibration, magnetization, and by  
0715 a narrow distribution of particles' size. ADMFBs, currently subjects of active  
0716 development, need to be envisioned as part of a CCS looping system to model  
0717 and implement the necessary updates to their functioning modes. The increase  
0718 of sorbent adsorption capacity will also improve separation.

0719 Regardless to replacement strategy, industrial implementation of solid sor-  
0720 bents  $\text{CO}_2$  capture needs much longer material characterization tests than the  
0721 ones currently available, which are limited to few tens of cycles. Thousands of  
0722 cycles will be necessary in order to explore sorbent degradation, presently un-  
0723 known beyond a few percent drop from fresh capacity for the most degradation-  
0724 prone materials, and completely unknown for the most resilient ones.

## 0725 0726 **9. Acknowledgments**

0727  
0728 The authors are thankful to Prof. Z. Xiao Guo, University College London,  
0729 and to Profs. Colin Snape and Hao Liu, University of Nottingham, for useful  
0730 suggestions and discussions. This work was supported by EPSRC Research  
0731 Grant EP/J020745/1.  
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