POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

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Tesi di Laurea Magistrale

Evaluation of the CO_2 capture and storage capacities of building materials

Relatori

prof.ssa Stefania Specchia
prof. Jean Marc Christian Tulliani

Candidato

Antonello Tangredi

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I. Introduzione

Questo lavoro si sviluppa attorno allo studio del processo di solubilizzazione dell'anidride carbonica in diverse formulazioni di bitume e di materiali bituminosi, attraverso la caratterizzazione della quantità di CO_2 trattenuta dai vari materiali oggetto dell'analisi e la valutazione di come questa quantità cambi al variare della pressione durante il processo di carbonatazione.

I principali elementi che si vogliono caratterizzare sono:

- le capacità massime di CO_2 per ciascuna formulazione di bitume o di materiale bituminoso in esame, a differenti condizioni di pressione;
- l'evoluzione nel tempo della quantità di CO_2 disciolta, in modo da caratterizzare la cinetica del processo di solubilizzazione;
- l'evoluzione nel tempo della quantità di CO_2 rilasciata quando il bitume carbonato è esposto all'aria libera, in modo da caratterizzare il processo di rilascio di CO_2.

Il lavoro è suddiviso in tre fasi sperimentali:

Nella prima fase, i campioni sono sottoposti a condizioni di temperatura e pressione ambiente (20 °C, $P = P_{atm}$), per quantificarne le capacità massime in CO_2 e la cinetica dei processi di solubilizzazione e di rilascio di questo gas. Durante questo primo gruppo di esperienze viene caratterizzato il potenziale di ritenzione naturale in CO_2 di questi materiali. L'analisi è realizzata seguendo una semplice procedura sperimentale in cui i campioni sono posti all'interno di una cella cilindrica soggetta ad una portata costante di anidride carbonica, controllata per mezzo di due flussimetri all'entrata e all'uscita della cella.

La quantità di CO_2 trattenuta dal campione può essere quantificata in due modi: osservando la variazione in massa dei campioni e analizzando la differenza tra le due portate massiche indicate dai due flussimetri posti a monte e a valle della cella sperimentale. Ciononostante, per i materiali in questione, le quantità di CO_2 trattenute sono relativamente piccole, abbastanza piccole da non essere quantificabili osservando la differenza tra le due portate. A causa di ciò, la semplice analisi gravimetrica è la sola procedura sperimentale utilizzata in questa fase del lavoro per caratterizzare il sistema, in termini di capacità massima e di cinetica dei processi di solubilizzazione e di rilascio di CO_2.

Nella seconda fase del lavoro, il sistema viene sottoposto a condizioni di pressione più elevata, nell'intervallo 1-20 bar. Anche in questa seconda fase dello studio vengono caratterizzate sia le capacità massime dei vari materiali, sia la cinetica dei processi di solubilizzazione e di rilascio di CO_2.

Nella terza fase del lavoro, i campioni di bitume carbonato in esame vengono sottoposti a condizioni di temperatura elevata (fino a 160 °C), e i gas rilasciati in seguito al riscaldamento sono prelevati e analizzati per mezzo della cromatografia in fase gassosa con rilevatore a ionizzazione di fiamma (GC-FID), con l'obiettivo di definire la natura dei componenti volatili rilasciati nel momento in cui le diverse formulazioni di bitume carbonato sono esposte a temperature superiori alla temperatura ambiente.

II. Contesto e definizioni

Con l'acronimo CCUS (*Carbon Capture, Utilization and Storage*) si indica un insieme di processi che consistono nella cattura del diossido di carbonio, nel suo trasporto verso un punto di immagazzinamento e nell'accumulo di tale gas in un materiale o sistema che ne permetta lo stoccaggio, con lo scopo di utilizzare ulteriormente la CO_2 o semplicemente di evitare il suo rilascio nell'atmosfera.

Svariati processi sono stati ideati ed implementati per lo stoccaggio permanente dell'anidride carbonica, tra cui lo stoccaggio in strutture geologiche sotterranee con caratteristiche idonee al confinamento, e lo stoccaggio in forma solida per reazione chimica della CO_2 con ossidi metallici, che porta alla formazione di carbonati stabili.

L'utilizzo di materiali bituminosi come mezzi in cui solubilizzare e stoccare la CO_2 è ampliamente discusso in letteratura in relazione ad alcuni importanti applicazioni pratiche relative ai processi di estrazione del petrolio.

Nell'attuale panorama energetico e geopolitico in cui il cambiamento climatico è diventato oggetto di intensa discussione e ricerca, le tecnologie conosciute sotto l'acronimo CO_2-EOR (*CO_2 injection Enhanced Oil Recovery*) vengono considerate particolarmente interessanti. Quando iniettata nel giacimento petrolifero, l'anidride carbonica si diffonde nell'olio greggio, causando una riduzione della viscosità dello stesso. Il greggio con viscosità ridotta può quindi essere pompato nel pozzo, ed estratto con un consumo inferiore d'energia.

Una strategia per la riduzione delle emissioni di gas serra che combini lo stoccaggio di CO_2 con la tecnologia di Recupero Forzato di Idrocarburi appare particolarmente interessante, in quanto permette di associare i costi relativi ai due singoli processi e di massimizzarne i possibili guadagni (il valore associato al greggio prodotto e i crediti di carbonio) [60]. Tale tecnologia di estrazione forzata sta diventando sempre più applicata ed importante nel panorama energetico mondiale, per questo motivo una caratterizzazione del fenomeno fisico-chimico di solubilizzazione della CO_2, alla base di tali operazioni, è oggetto di molte ricerche disponibili in letteratura.

L'interesse scientifico attorno a questo processo non è associato alla comprensione completa dei meccanismi alla base del fenomeno o ad una sua quantificazione dettagliata, ma più che altro alle conseguenze pratiche che la solubilizzazione di tale gas nei greggi pesanti ha sulle proprietà fisiche e reologiche di questi ultimi.

Il lavoro presentato in questa tesi si concentra sulla possibilità di usare i materiali oggetto di questo studio (due formulazioni di bitume e un conglomerato bituminoso), come materiali per lo stoccaggio di anidride carbonica, e di esplorare la possibilità di uno stoccaggio permanente. Lo scopo di questo lavoro è quello di caratterizzare le capacità massime di tali materiali a diverse condizioni di pressione, di analizzare la termodinamica e la cinetica dei fenomeni di solubilizzazione e di rilascio di CO_2, e di valutare se i materiali in questione possano essere effettivamente considerati buoni candidati per lo stoccaggio di anidride carbonica.

Il bitume è un derivato liquido o semi-solido del petrolio, altamente viscoso, nero e appiccicoso. È necessario distinguere i bitumi naturali, che si presentano come sacche nel sottosuolo o affioramenti superficiali diffusi soprattutto in Canada, Messico, Venezuela e Cuba, dai bitumi ottenuti dalla distillazione frazionata del greggio a 525 °C, indicati come "bitumi raffinati".

Non è semplice effettuare una caratterizzazione chimica dettagliata del bitume. Generalmente un campione di greggio può contenere tra le 10^5 e le 10^6 molecole diverse [21]. A causa di questa complessità, una caratterizzazione dell'intera composizione chimica è impossibile. Ciononostante, è possibile operare una delineazione generica dei diversi componenti attraverso un processo di separazione del bitume in diverse frazioni, per mezzo di varie tecniche (adsorbimento/desorbimento, solubilizzazione in diversi solventi, distillazione) [21].

I componenti del bitume possono essere separati in quattro grandi famiglie chimiche con le caratteristiche seguenti [40]:

- Composti saturi: peso molecolare tra 500 u e 800 u, solidi o liquidi molto viscosi.
- Aromatici: peso molecolare tra 500 u e 900 u, liquidi viscosi dal colore marrone-bruno.
- Resine: peso molecolare tra 900 u e 1300 u, solidi o semi-solidi bruni, solubili nei solventi paraffinici, adesivi e polari.
- Asfalteni: peso molecolare molto elevato, tra 1000 u e 50000 u, solidi o semi-solidi amorfi, neri o marroni, generalmente ottenibili per precipitazione quando il bitume è dissolto in solventi paraffinici.

Una rappresentazione schematica e semplificata della generica composizione del bitume è disponibile in figura II.1.

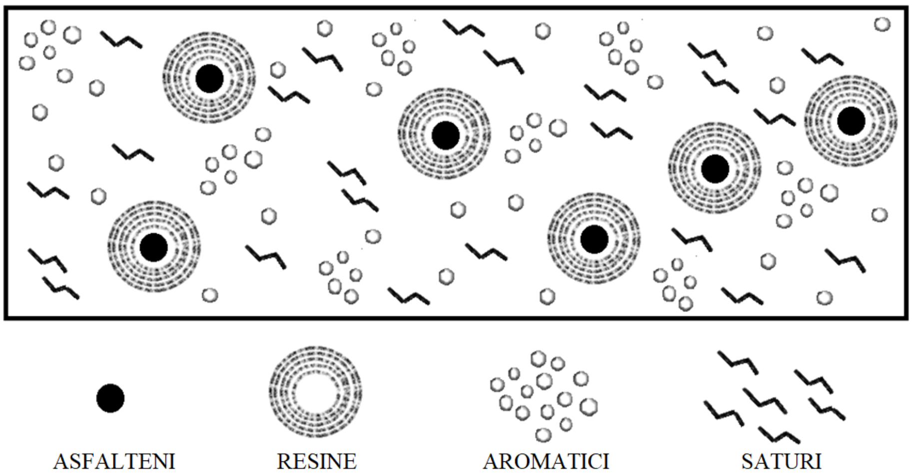


Figura II.1: Composizione colloidale del bitume, tratta da Nicholls [40], con modifiche.

Il bitume è composto predominantemente da molecole di idrocarburi e da una minore quantità di composti contenenti eteroatomi, la maggior parte dei quali contiene zolfo, azoto o ossigeno. Il bitume contiene però anche tracce di specie metalliche (vanadio, nickel, ferro, ecc.). [54].

Con l'acronimo RAP (*Reclaimed Asphalt Pavements* o *Recycled Asphalt Pavements*), in italiano *conglomerati bituminosi riciclati*, si indica una miscela di aggregati inerti e di collanti bituminosi utilizzati per la realizzazione di superfici carrabili, rimossi e riciclati [49]. I RAP sono il risultato del processo di riciclo del conglomerato bituminoso (materiale composito costituito da inerti, tra cui sabbia, povere di cemento, pietrisco, ecc., tenuti insieme da strati compattati di bitume).

III. Risultati della ricerca bibliografica

Il principale interesse pratico dei lavori che studiano il processo di solubilizzazione della CO_2 nei materiali bituminosi, consiste nella caratterizzazione delle proprietà fisiche e reologiche delle miscele bitume-CO_2, in particolare della solubilità della CO_2 e della viscosità del bitume carbonato.

La tabella III.1 riassume i valori di solubilità massima trovati in letteratura per diversi tipi di bitume, espressi in frazione molare percentuale e frazione massica percentuale, con le corrispondenti condizioni di pressione e temperatura. Osservando la tabella, si può notare come sia possibile dissolvere quantità considerevoli di anidride carbonica nel bitume, spesso fino al 60 mol% (9-13 wt%), a temperature prossime alla temperatura ambiente, ma a condizioni di pressione relativamente elevata (tra 60 e 110 bar).

Tabella III.1: Valori di solubilità massima per diversi tipi di bitume.

Tipo di bitume	Massima concentrazione molare, mol%	Massima concentrazione massica, wt%	Temperatura, °C	Pressione, Mpa	Fonte
Cold Lake	63	13.43	15	10.95	*Mehrotra and Svrcek [35]*
Athabasca	57	8.93	24	6	*Svrcek and Mehrotra [52]*
Peace River	59	10.72	-3.9	6.1	*Mehrotra and Svrcek [35]*
Wabasca	60	12.88	21,9	5.9	*Mehrotra and Svrcek [35]*
Tar Sand Triangle	46	5.08	85	5.52	*Deo, Wang and Hanson [13]*
PR Spring	47	6.73	85	5.52	*Deo, Wang and Hanson [13]*

Generalmente, i lavori utilizzati in questa fase di ricerca bibliografica [13] [17] [32] [33] [35] [38] [52] [62] analizzano il sistema bitume-CO_2 a pressioni relativamente alte (decine di bar), in quanto analizzano tale sistema con lo scopo di caratterizzare il processo di recupero forzato di idrocarburi attraverso l'iniezione di CO_2. In questo tipo di processo, infatti, vengono iniettate grandi quantità di CO_2 gassosa nel giacimento del greggio, portando la pressione a diversi Mpa, con lo scopo di massimizzarne la percentuale diffusa nel greggio, ridurre il più possibile la viscosità di quest'ultimo per facilitarne in processo di estrazione.

Un altro gruppo di studi [46][53][56][58][59][63] si concentra sulla caratterizzazione e quantificazione della diffusività dell'anidride carbonica nel bitume, fornendo informazioni sul fenomeno di solubilizzazione della CO_2 nel bitume da un punto di vista "cinetico", ossia in termini di evoluzione nel tempo della quantità di CO_2 diffusa, fino al raggiungimento dell'equilibrio termodinamico. Questi risultati sono spesso presentati sotto forma di grafici di caduta di pressione o di quantità di CO_2 solubilizzata in funzione del tempo. Anche nel caso di questo gruppo di studi, le pressioni investigate sono relativamente elevate (almeno 20 bar), e pertanto, sebbene i risultati siano interessanti, non forniscono una caratterizzazione completa del sistema in condizioni prossime alle condizioni ambiente.

La solubilità della CO_2 nel bitume a pressione ambiente non è stata caratterizzata in nessuno studio disponibile durante la stesura di questo lavoro, in quanto pochissime informazioni sono disponibili in letteratura in relazione a tale fenomeno in condizioni di pressione relativamente bassa. Ciononostante, Apeagyei et Al. [2] analizzano il sistema in condizioni prossime alle condizioni ambiente. Tale lavoro analizza la cinetica del processo di diffusione di CO_2 nel bitume a 20 °C e 2.75 bar. In queste condizioni sperimentali, dopo 150-180 ore di esposizione all'anidride carbonica, due diverse formulazioni di bitume trattengono rispettivamente lo 0.41 wt% e lo 0.33 wt% di CO_2. Questi risultati delineano una capacità di stoccaggio di CO_2 relativamente limitata in condizioni di bassa pressione.

Questo studio fornisce anche informazioni sulla stabilità della miscela bitume-CO_2, che è stata caratterizzata analizzando il fenomeno di rilascio di CO_2 dal bitume carbonato quando quest'ultimo è esposto all'aria in condizioni di temperatura e pressione ambiente (20 °C e 1 atm). La caratterizzazione della stabilità del bitume carbonato è particolarmente importante in quanto permette di valutare se tali materiali sono buoni candidati per uno stoccaggio di CO_2 a lungo termine. Una analisi di questo fenomeno (degassaggio di CO_2 dal bitume carbonato) non è presente in nessun altro dei lavori analizzati in questa fase di ricerca bibliografica. Secondo i risultati di Apeagyei et Al. [2], i tempi necessari per un rilascio sostanziale della CO_2 solubilizzata nel bitume carbonato sono dell'ordine di alcuni giorni. Dopo oltre 200 ore di esposizione all'aria in condizioni di pressione e temperatura ambiente, il bitume carbonato trattiene una concentrazione massica residua di CO_2 dello $0.065 \pm 0.009\%$.

I dati sperimentali ottenuti in questo studio sono stati utilizzati per lo sviluppo di un semplice modello cinetico basato sul modello di Peleg [42], un modello empirico non esponenziale a due parametri, descritto dalle equazioni 2.5 e 2.6. Tale equazione permette di modellizzare con successo la diffusione del vapore d'acqua nel bitume, ed è stato applicato con successo anche per predire la solubilizzazione dell'anidride carbonica in tale materiale [2].

Li et Al. [29] investigano la natura delle interazioni alla base del fenomeno di solubilizzazione di anidride carbonica nel bitume, utilizzando il metodo di dinamica molecolare per costruire i sistemi di associazione di tre tipi di sostanze: resina, asfaltene, resina-asfaltene. I risultati relativi alle energie di interazione ottenuti in questo studio permettono di concludere che le interazioni tra le molecole di CO_2 e i sistemi simulati implicano la formazione di legami chimici relativamente forti.

Infine, un rapporto tecnico di Sutter et Al. [51], fornisce i dettagli di un programma di temperatura per la caratterizzazione dei componenti volatili rilasciati in seguito al riscaldamento di diversi campioni di bitume attraverso la tecnica analitica nota come cromatografia in fase gassosa (GC). Tale programma è stato analizzato e adattato per la realizzazione dell'ultima fase di questo lavoro, che consiste proprio nella caratterizzazione per mezzo della GC dei componenti rilasciati in seguito alla decomposizione termica del bitume carbonato.

IV. Complesso sperimentale, materiali e metodi

Gli esperimenti relativi alle prime due fasi di questo lavoro sono stati realizzati utilizzando il complesso sperimentale schematizzato in figura IV.1. Le due fasi del lavoro (a pressione ambiente e a pressioni superiori alla pressione ambiente) hanno richiesto l'applicazione di diverse condizioni sperimentali, e per questo motivo due variazioni dello schema sperimentale originale sono state utilizzate, applicando le opportune modifiche a livello della cella sperimentale.

Il complesso sperimentale schematizzato in figura IV.1 consiste in una cella cilindrica in plexiglass alta 15 cm, con un diametro di 10 cm, posta tra due basi anch'esse cilindriche in acciaio inossidabile. A monte e a valle della cella sono connessi due flussimetri che permettono di misurare la portata volumica e massica dell'anidride carbonica che entra ed esce dalla cella. La cella è provvista di un sistema per la misura istantanea della temperatura, che consiste in una termocoppia di tipo K, e un trasmettitore piezoresistivo per la misura della pressione. Tra la cella sperimentale e il secondo flussimetro sono presenti due filtri: il primo permette di trattenere l'eventuale acqua presente nella corrente gassosa uscente, e il secondo permette di filtrare eventuali particelle solide che danneggerebbero il flussimetro.

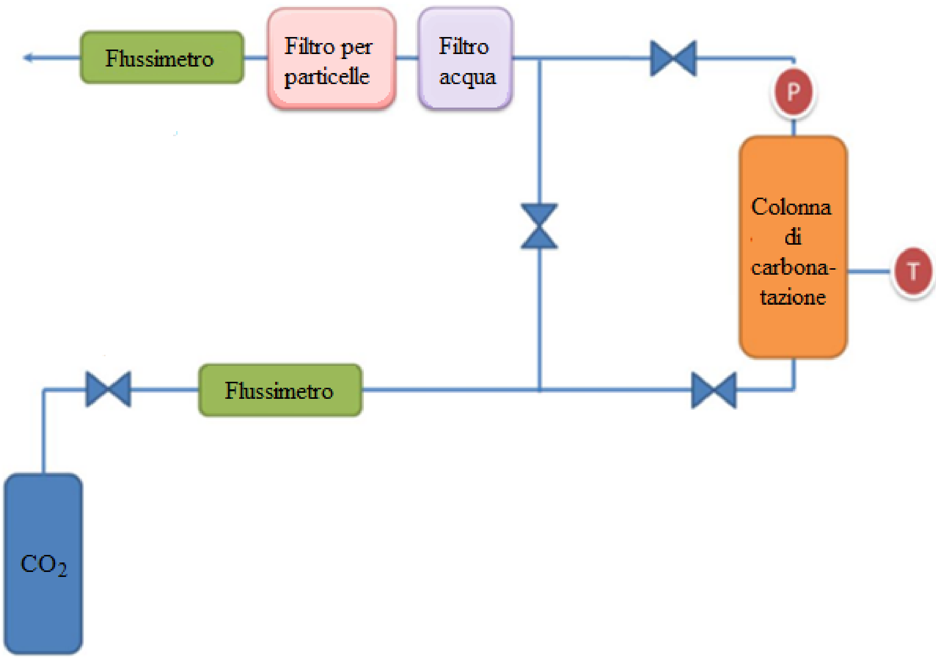


Figura IV.1: Schema del complesso sperimentale utilizzato nelle prime due fasi del lavoro.

I campioni all'interno della cella sono sottoposti ad una portata di CO_2 entrante ed uscente costante e pari a 10 ml/min. Il ricambio costante di CO_2 all'interno della cella permette di avere una atmosfera dalle caratteristiche invariate, e quindi una concentrazione costante di CO_2 all'interfaccia bitume-gas.

Le condizioni di temperatura all'interno del locale variano tra 19 °C e 21.5 °C.

Il metodo scelto per caratterizzare il processo di solubilizzazione di CO_2 nel bitume è una tecnica gravimetrica che consiste nella misura accurata della massa dei campioni prima e dopo l'inserimento nella cella per esporli all'atmosfera di anidride carbonica per un certo intervallo di tempo.

La massa dei campioni è misurata per mezzo di una bilancia di precisione (risoluzione di 10^{-4} g) posta all'esterno della cella sperimentale; pertanto, per misurare la variazione in massa è necessario estrarre i campioni dalla cella. Questo tipo di misura ex-situ potrebbe risultare problematica, in quanto per estrarre i campioni dalla cella è necessario aprirla, variando le condizioni sperimentali al suo interno e dovendo poi attendere alcuni istanti per ristabilire i valori prefissati. Ciononostante, la prima fase di questo studio non richiede alcuna pressurizzazione della cella sperimentale, e pertanto le operazioni di estrazione dei campioni, misura e re-inserimento nella cella richiedono pochi secondi e non disturbano particolarmente le condizioni sperimentali del sistema investigato.

Ciò è stato verificato comparando la variazione in massa di alcuni campioni che sono stati lasciati nella cella durante l'intero processo di solubilizzazione senza alcuna estrazione intermedia, con le variazioni in massa di altri campioni per cui sono state misurate le masse in maniera progressiva, estraendo e re-inserendo i campioni più volte. I risultati sono comparabili e la differenza fra i due gruppi di valori cade all'interno dell'errore sperimentale, mostrando come il processo naturale di rilascio di CO_2 che avviene quando i campioni vengono prelevati per la misura della massa, non ha un effetto significativo sui risultati sperimentali.

La seconda fase di questo lavoro, che richiede pressioni più elevate, è stata realizzata utilizzando un altro tipo di cella sperimentale: il reattore di 7.6 L in acciaio inossidabile, fornito da *Parr instruments* (modello 4666), mostrato in figura IV.2. Questo dispositivo, che sostituisce la cella in plexiglass descritta precedentemente ed utilizzata nella prima fase, ha una pressione di lavoro massima di 130 bar e una temperatura di lavoro massima di 350 °C, ben al di sopra delle condizioni sperimentali applicate in questo lavoro.

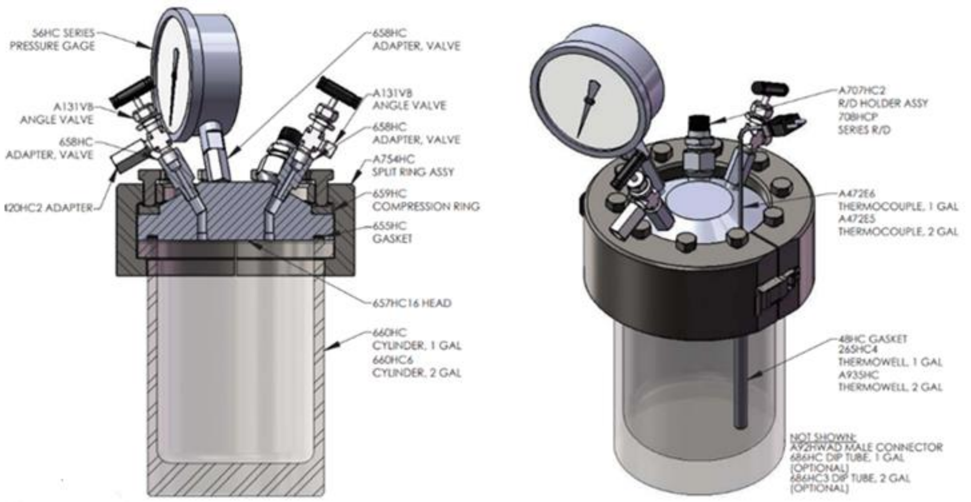


Figura IV.2: Schema del reattore Parr Instruments - serie 4666 [41].

Nella terza ed ultima fase del lavoro, ossia l'analisi per mezzo della cromatografia in fase gassosa, il reattore viene provvisto di un sistema di riscaldamento (una camicia cilindrica posta attorno al reattore), associato ad un sistema di controllo della temperatura. La gas cromatografia è realizzata utilizzando un cromatografo *PerkinElmer Clarus® 590*. I campioni di gas e componenti volatili rilasciati in seguito al riscaldamento dei campioni sono prelevati dal reattore pressurizzato e introdotti all'interno di sacchetti di campionamento in Tedlar. Per trasferire il contenuto dei sacchetti alla porta di iniezione del cromatografo, è stata realizzata una micro-estrazione in fase solida (SPME), che ha permesso di estrarre gli analiti organici facendoli adsorbire su una fibra in silicio rivestita di una appropriata fase stazionaria liquida. Nel momento in cui la fibra viene inserita nella porta di iniezione e scaldata, gli analiti si desorbono all'interno della colonna del cromatografo.

I materiali selezionati per questo lavoro consistono in tre tipi di campioni, due formulazioni di bitume (una classica ed una modificata per mezzo dell'aggiunta di alcuni additivi), e un conglomerato bituminoso, che consiste in una miscela di vari materiali inerti dalla granulometria variabile (da granuli molto fini che costituiscono una fine polvere sottile fino a pezzi con diametro caratteristico dell'ordine di 2-3 cm) rivestiti da un sottile strato di bitume.

I campioni realizzati per questo lavoro sono stati preparati seguendo una particolare procedura. I campioni di conglomerato bituminoso sono stati setacciati diverse volte per selezionare il materiale con granulometria compresa tra 1 mm e 2 mm. 50 g di conglomerato con questa granulometria sono stati versati all'interno di un contenitore discoidale in vetro temprato di 8.5 cm di diametro.

I campioni di bitume di entrambe le formulazioni sono realizzati sotto forma di strati sottili. I campioni forniti risultano avere una viscosità particolarmente alta a temperatura ambiente, complicandone la manipolazione. Per la preparazione di ciascun campione, circa 15 g di bitume sono stati posti all'interno dei dischi in vetro di 8.5 cm di diametro, i contenitori con i pezzi di bitume all'interno sono stati quindi scaldati a circa 160 °C, temperatura ideale per assicurare il rammollimento di queste formulazioni di bitume e la formazione di strati sottili di bitume spessi 4-5 mm.

V. Risultati della prima fase sperimentale

La prima fase sperimentale di questo lavoro è stata realizzata inserendo i campioni all'interno di una cella cilindrica in plexiglass non pressurizzata, soggetta ad un flusso costante di CO_2 di 10 ml/min. Pertanto, i campioni sono stati esposti ad una atmosfera di anidride carbonica a pressione costante pari alla pressione atmosferica.

I risultati dell'esposizione dei tre tipi di materiali a tali condizioni sperimentali per una durata di 168 ore (1 settimana) sono riportati in figura V.1. I valori presentati in figura corrispondono alla media aritmetica dei risultati ottenuti dalle diverse campagne sperimentali, e le barre d'errore che accompagnano i punti sperimentali corrispondono all'intero intervallo di valori (minimo-massimo) ottenuti per ciascuna formulazione.

Sebbene le quantità di CO_2 solubilizzata siano molto limitate in termini assoluti, il bitume modificato presenta dei valori di concentrazione massica tra lo 0.39% e lo 0.47%, circa quattro volte maggiore rispetto al valore medio associato al bitume classico, la cui concentrazione varia tra lo 0.09% e lo 0.13% in massa. Un altro risultato interessante è la quantità particolarmente bassa di CO_2 adsorbita dal campione di conglomerato bituminoso. Infatti, questo materiale può adsorbire poco più dello 0.01% in massa di anidride carbonica, una quantità così limitata da escludere qualunque applicazione pratica.

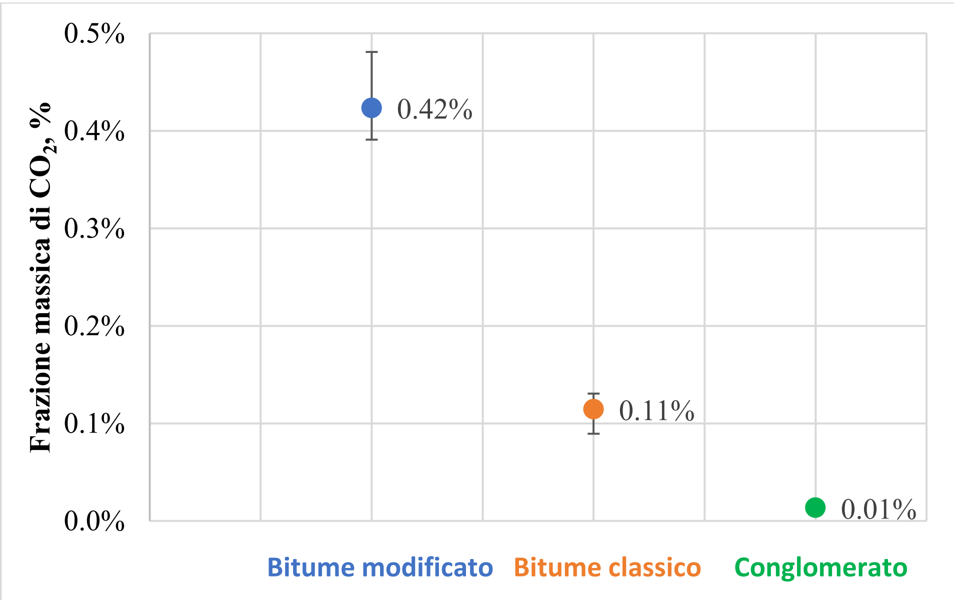


Figura V.1: Frazione massica di CO_2 (%) dopo 168 ore di esposizione in una cella con una atmosfera di CO_2 a pressione ambiente.

La cinetica del processo di solubilizzazione di CO_2 da parte delle due formulazioni di bitume in esame è stata caratterizzata misurando progressivamente la variazione in massa dei campioni inseriti nella cella sperimentale durante l'intera durata dell'esperimento, e tracciando la variazione percentuale in massa di entrambi i bitumi in funzione del tempo. Questo procedimento è stato applicato a diversi campioni per entrambe le formulazioni utilizzate.

Non è stato possibile effettuare lo stesso tipo di caratterizzazione per i campioni di conglomerato bituminoso, per i quali sono stati ottenuti valori inconcludenti, probabilmente dovuti al fatto che le quantità adsorbite sono così limitate da essere dello stesso ordine di grandezza dell'errore sperimentale: un eventuale desorbimento relativo alla manipolazione dei campioni durante la misura della massa, anche minimo, ha effetti negativi sulla qualità dei risultati ottenuti.

I punti blu nelle figure V.2 e V.3 mostrano l'evoluzione della concentrazione massica media di CO_2 in funzione del tempo (numero di ore passate dall'inizio dell'esposizione), per entrambi i campioni di bitume. Dopo 168 ore di esposizione diretta all'atmosfera di CO_2, l'uptake massico dei campioni di bitume modificato varia tra lo 0.40% e lo 0.47%, mentre per i campioni di bitume classico varia tra lo 0.10% e lo 0.13%. Questa variabilità è dovuta ad una serie di fattori non controllabili durante la realizzazione delle esperienze, in primis la temperatura non costante del locale in cui è posto il complesso sperimentale, ma anche le piccole variazioni in massa dei vari campioni e la posizione all'interno della cella sperimentale.

Utilizzando i dati appena presentati, è possibile realizzare un modello della cinetica del processo di diffusione/solubilizzazione della CO_2 per le due formulazioni di bitume. Il modello utilizzato è il modello di Peleg [42], descritto dalle equazioni 2.5 e 2.6. Nelle figure V.2 e V.3 è possibile osservare in arancione le curve costruite utilizzando il modello di Peleg.

Il processo di solubilizzazione della CO_2 in entrambe le formulazioni di bitume segue un andamento a saturazione: il processo inizia con una certa velocità, che diminuisce progressivamente fino a che la concentrazione massica di CO_2 non raggiunge un valore per il quale la cinetica è nulla e il processo di diffusione si arresta. In termini grafici il rallentamento della cinetica del processo di solubilizzazione si traduce in una curva che cresce sempre più lentamente, fino a raggiungere un plateau corrispondente alla capacità massima di equilibrio.

La curva relativa al bitume classico, in figura V.3, cresce più rapidamente e raggiunge il valore di capacità massima in meno tempo rispetto alla curva associata al bitume modificato, in figura V.2.

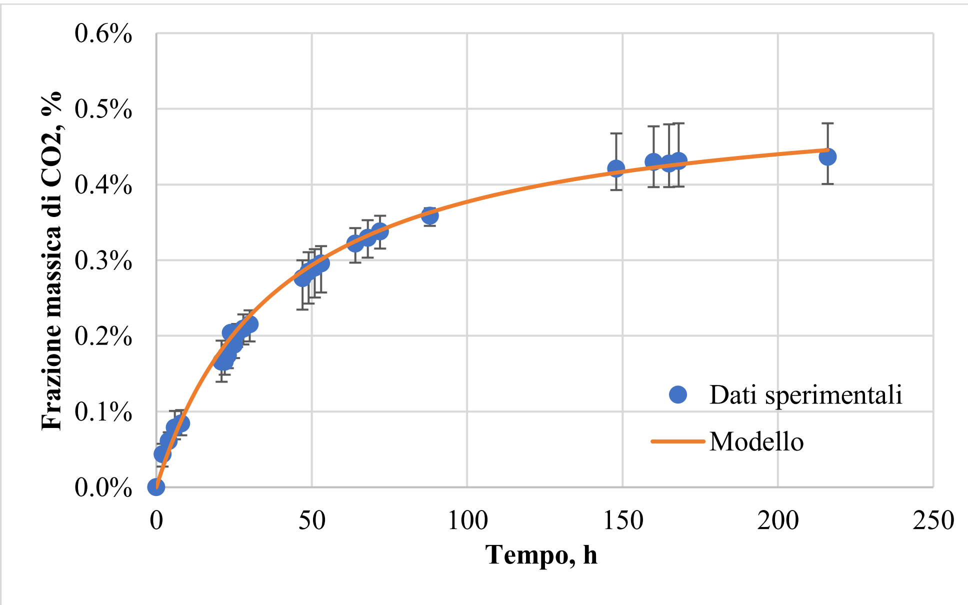


Figura V.2: Frazione massica di CO_2 media per i campioni di bitume modificato. In blu, punti sperimentali; in arancione, curva ottenuta con il modello di Peleg.

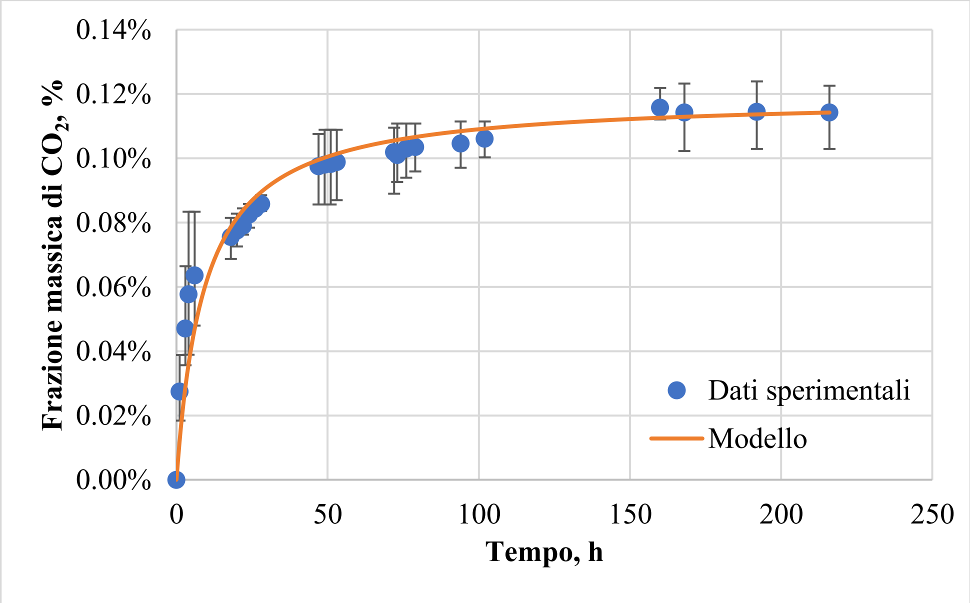


Figura V.3: Frazione massica di CO_2 media per i campioni di bitume classico. In blu, punti sperimentali; in arancione, curva ottenuta con il modello di Peleg.

Nella tabella V.1 sono riportati i valori dei parametri del modello calcolati per entrambe le formulazioni di bitume. Secondo il modello, il valore massimo di concentrazione massica del bitume modificato è pari a circa lo 0.53%. Ciò significa che i campioni di bitume modificato potrebbero contenere delle quantità di CO_2 superiori rispetto ai valori ottenuti dopo 168 ore di esposizione (in media, lo 0.431%), ma per fare ciò sarebbe necessario esporre i campioni per dei tempi relativamente lunghi, in quanto il modello predice il raggiungimento di una concentrazione dello 0.50% dopo 720 ore (un mese), e dello 0.52% dopo 2600 ore (tre mesi e mezzo).

Tabella V.1: Parametri del modello di Peleg calcolati a partire dai dati sperimentali

Tipo di bitume	**C_1, h**	**C_2**	**k, h^{-1}**	**x_e**
Modificato	7576.01	189.39	4.735	0.528 %
Classico	7780.87	839.45	90.565	0.119%

Il modello associato al bitume classico predice un valore di concentrazione di equilibrio pari allo 0.119% in massa, molto vicino al valore medio osservato dopo una settimana di esposizione (0.115%), indicando che già dopo 168 ore di esposizione, questa formulazione di bitume è molto vicina al limite massimo di equilibrio. In questo caso la cinetica del processo è maggiore, in quanto la curva raggiunge valori prossimi al plateau massimo in un tempo inferiore rispetto alla curva relativa al bitume modificato. Questo dettaglio si traduce matematicamente nel valore del parametro di costante cinetica k, pari a circa 90 h^{-1} nel caso del bitume classico, e molto più piccolo nel caso del bitume modificato (circa 5 h^{-1}).

La maggior parte dei campioni utilizzati per caratterizzare il processo di solubilizzazione, sono stati poi utilizzati per caratterizzare il processo inverso, ossia il graduale rilascio di CO_2 da parte dei campioni carbonati quando questi vengono esposti all'aria in condizioni di pressione e temperatura ambiente.

I campioni precedentemente posti all'interno della cella sperimentale in cui è presente l'atmosfera di CO_2, sono stati prelevati, pesati, e poi inseriti all'interno di un contenitore cilindrico con un foro nella parte superiore che permette la comunicazione con l'atmosfera esterna e lo scambio d'aria. I campioni non sono stati semplicemente posti all'esterno, per evitare l'eventuale contaminazione da parte di materiale estraneo, come la polvere. Nel contenitore è presente del materiale igroscopico (gel di silice), per mantenere il tasso di umidità basso ed evitare la possibilità che il vapore d'acqua presente nell'aria condensi sui campioni invalidando la caratterizzazione del processo.

Per caratterizzare il comportamento generale di entrambe le formulazioni di bitume carbonato, la quantità di CO_2 trattenuta (espressa come frazione percentuale del valore iniziale, misurato alla fine del processo di solubilizzazione) è stata tracciata in funzione del tempo, realizzando curve che iniziano dal 100% (il valore iniziale massimo) e terminano ad un valore finale di equilibrio corrispondente alla frazione di CO_2 trattenuta dopo 216 ore di esposizione all'aria libera.

Come è possibile vedere in figura V.4, dopo 216 ore il bitume modificato trattiene in media l'81% della CO_2 precedentemente solubilizzata. Considerando che a questa formulazione di bitume è associato una concentrazione di CO_2 pari allo 0.43 ± 0.04 % in massa, dopo 9 giorni di esposizione all'aria libera il materiale trattiene tra lo 0.32% e lo 0.39% in massa di CO_2, ossia circa cinque volte la concentrazione massica di anidride carbonica presente mediamente nell'aria (pari allo 0.063%) [16]. In figura V.5 è possibile osservare che il bitume classico dopo 216 ore di esposizione all'aria in condizioni ambiente trattiene circa il 32% della quantità originariamente trattenuta.

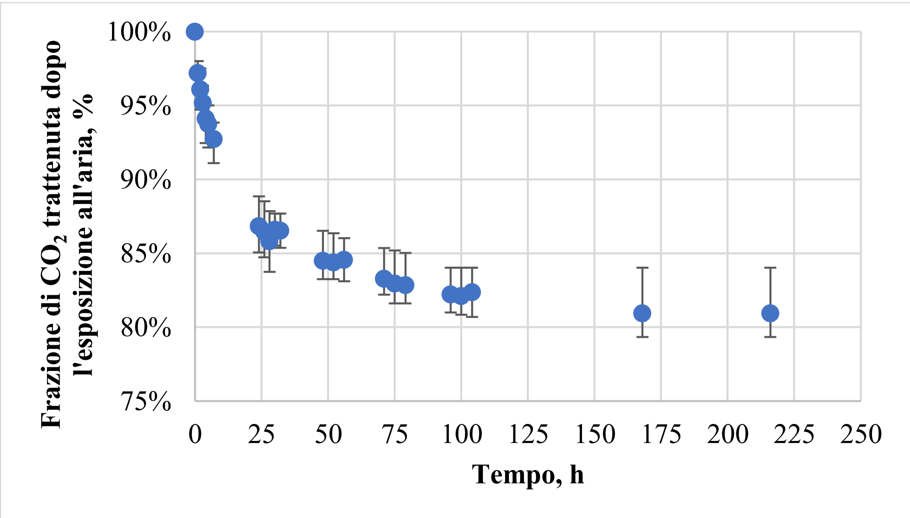


Figura V.4: Frazione della quantità di CO_2 trattenuta dal bitume modificato dopo l'esposizione all'aria in funzione del tempo.

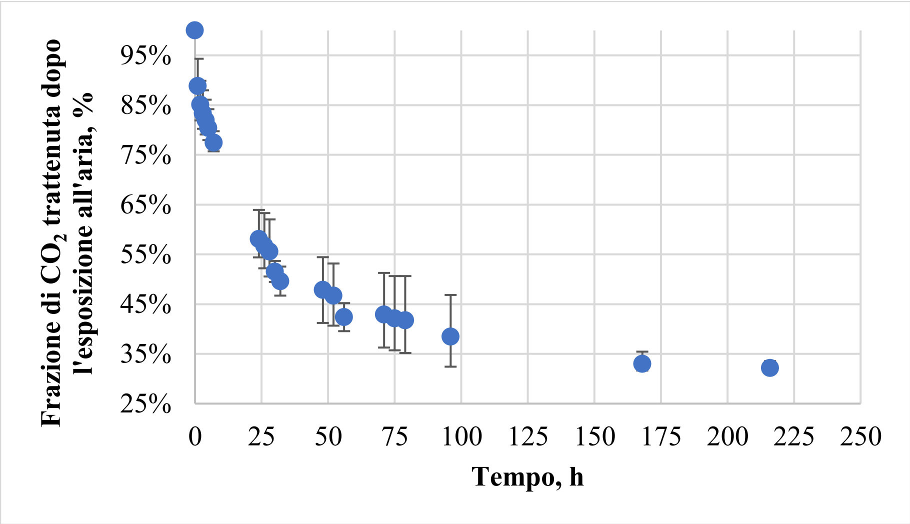


Figura V.5: Frazione della quantità di CO_2 trattenuta dal bitume classico dopo l'esposizione all'aria in funzione del tempo.

Tra le due formulazioni, il bitume modificato è l'unico materiale che può essere considerato come candidato per un ipotetico processo di sequestro della CO_2 dall'aria in queste condizioni sperimentali, nonostante le quantità in gioco siano molto ridotte.

VI. Risultati della seconda fase sperimentale

Nella seconda fase del lavoro, il processo di solubilizzazione di CO_2 da parte dei tre materiali descritti precedentemente è stato caratterizzato in condizioni di pressione superiore alla pressione atmosferica. Questa fase del lavoro è stata realizzata utilizzando come cella sperimentale il reattore di 7.6 L in acciaio inossidabile fornito da *Parr Instruments* e mostrato in figura IV.2. Il reattore è connesso alla bombola di CO_2 attraverso un tubo in acciaio. Un riduttore di pressione all'uscita della bombola permette di regolare la pressione del gas uscente. Il sistema sperimentale è stato caratterizzato a temperatura ambiente e nell'intervallo di pressione 1-10 bar (sono stati realizzati 5 gruppi di esperimenti, a 1.5 bar, 3 bar, 5 bar, 7 bar e 9 bar).

Il metodo selezionato per caratterizzare il processo di diffusione e solubilizzazione della CO_2 in condizioni di pressione superiore alla pressione atmosferica è ancora una volta il metodo gravimetrico, in quanto non è stato possibile monitorare direttamente l'evoluzione della pressione all'interno del reattore, poiché tali variazioni sono relativamente ridotte e non possono essere definite con accuratezza dall'osservazione del manometro analogico.

Per ogni gruppo di esperimenti, realizzato ad una specifica pressione, sono stati utilizzati almeno tre campioni di ciascun materiale, in modo da poter definire la variabilità sperimentale. In ciascuna esperienza i campioni sono posti all'interno del reattore in cui è presente una atmosfera di CO_2 sotto pressione, per 88 ore. Il tempo di esposizione limitato implica l'ottenimento di valori di concentrazione massica che non sono necessariamente prossimi alla capacità massima di equilibrio.

Le figure VI.1, VI.2 e VI.3 mostrano la concentrazione massica percentuale dopo 88 ore di esposizione ad una atmosfera di CO_2 a diverse pressioni, rispettivamente per il bitume modificato, il bitume classico, e il conglomerato bituminoso. Come è possibile vedere nelle figure VI.1 e VI.2, i punti sperimentali associati alla concentrazione massica di CO_2 dopo 88 ore di esposizione, sia nel caso del bitume modificato che nel caso del bitume classico, seguono un andamento lineare. Nel caso del conglomerato bituminoso invece l'andamento non è lineare e il valore di concentrazione percentuale si stabilizza attorno allo 0.1% già a 3 bar di pressione, e cresce limitatamente a pressioni più alte.

È possibile effettuare un confronto di questi dati sperimentali con i risultati di Apeagyei et Al. [2], nel quale il modello utilizzato (Peleg), permette di stimare una concentrazione tra lo 0.22% e lo 0.27% dopo 88 ore di esposizione. Tale valore è inferiore ai risultati del nostro lavoro (circa lo 0.41%), ma può essere considerato coerente, soprattutto se si considera che in questo lavoro sono state utilizzate delle formulazioni di bitume differenti e una pressione superiore rispetto a quelle del lavoro citato.

La curva relativa all'agglomerato bituminoso, in figura VI.3, cresce sempre più lentamente, raggiungendo una concentrazione massica dello 0.11%. a 9 bar. A 3 bar di pressione, la concentrazione del conglomerato è pari allo 0.09%, ossia circa un quarto del valore del bitume classico a parità di condizioni sperimentali. La quantità di CO_2 trattenuta è sicuramente maggiore rispetto a quella che sarebbe solubilizzata dalla sola frazione bituminosa del conglomerato, che costituisce una piccola frazione del materiale. Questo significa che anche la componente solida inerte del materiale partecipa al fenomeno di ritenzione di CO_2, probabilmente attraverso un processo fisico di adsorbimento, che sembra diventare importante nel momento in cui la pressione del sistema aumenta (poiché a pressione ambiente la quantità ritenuta è pari allo 0.01%, molto piccola, quasi trascurabile), ma che si stabilizza ad un valore massimo senza più aumentare con la pressione, forse a causa del raggiungimento della saturazione superficiale della componente solida.

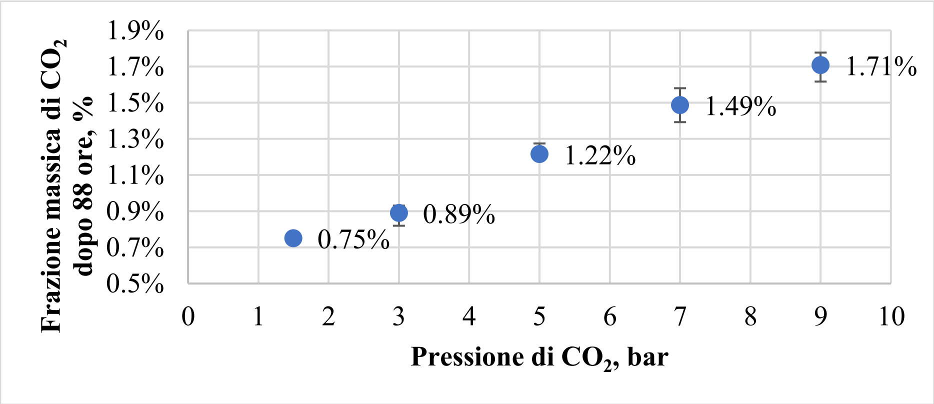


Figura VI.1: Frazione massica percentuale di CO_2 nel bitume modificato dopo 88 ore di esposizione.

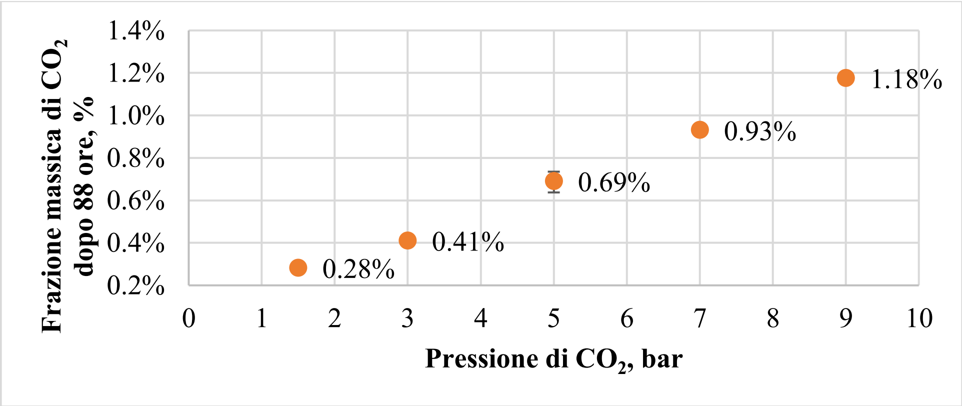


Figura VI.2: Frazione massica percentuale di CO_2 nel bitume classico dopo 88 ore di esposizione.

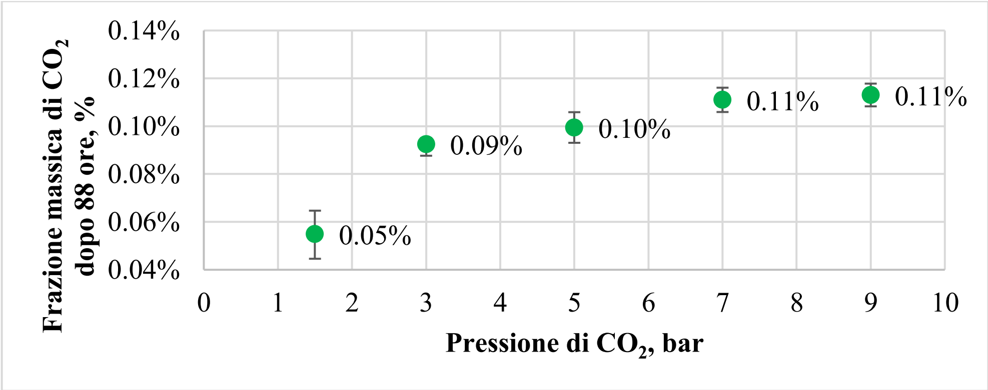


Figura VI.3: Frazione massica percentuale di CO_2 nel conglomerato bituminoso dopo 88 ore di esposizione.

La cinetica del processo di solubilizzazione a pressione superiore alla pressione atmosferica è stata definita monitorando progressivamente la massa dei campioni durante la durata dell'intero esperimento, per 160 ore. Questa caratterizzazione è stata realizzata a 3 bar di pressione e a 9 bar di pressione. I relativi risultati sono presentati in figura VI.4 e in figura VI.5.

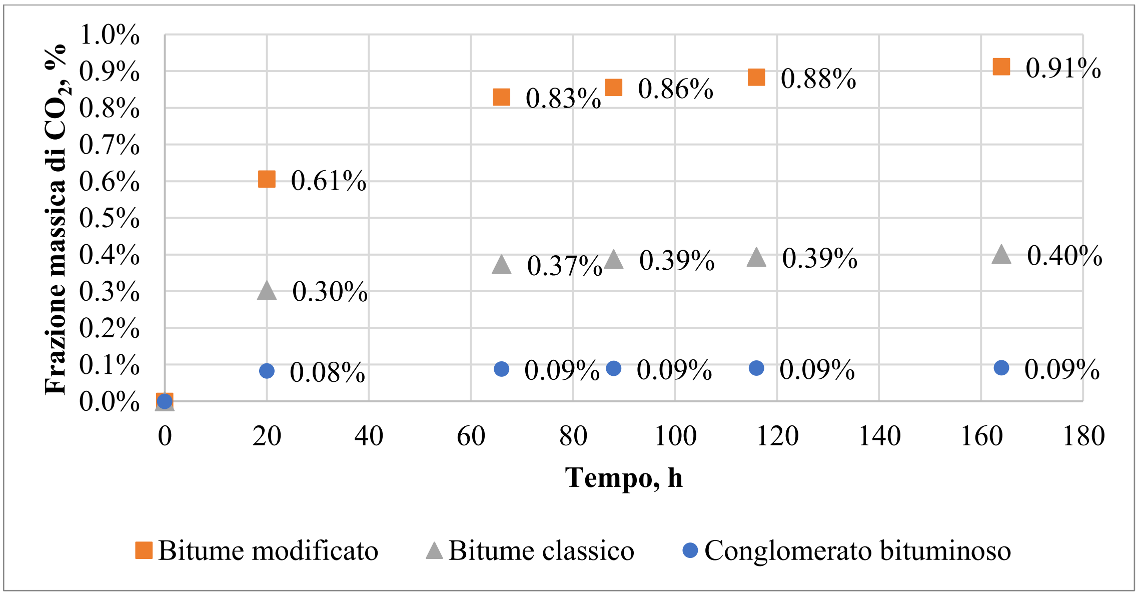


Figura VI.4: Frazione massica di CO_2 per i tre materiali investigati a 3 bar di pressione.

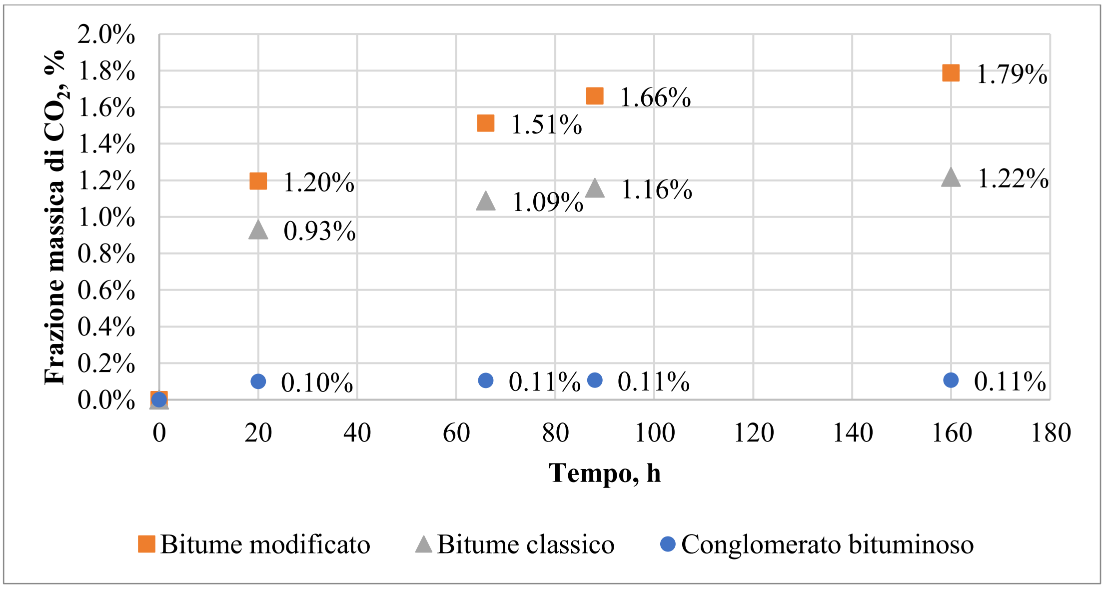


Figura VI.5: Frazione massica di CO_2 per i tre materiali investigati a 9 bar di pressione.

A differenza delle esperienze realizzate a pressione ambiente, per le quali il processo di misura richiede qualche decina di secondi, in questo caso la misura della massa richiede alcuni minuti, perché è necessario depressurizzare il reattore, aprirlo, estrarre i campioni, pesarli, inserirli nuovamente nel reattore, e ristabilire la pressione. Questo significa che durante la misura della massa una quantità non trascurabile di CO_2 potrebbe essere rilasciata dai campioni. Infatti, misurando progressivamente la massa dei campioni, è probabile che questi ultimi perdano una certa quantità di CO_2 solubilizzata, e quando questi vengono re-inseriti nel reattore, il fenomeno di solubilizzazione ricomincia, ma a partire da un valore inferiore rispetto a quello che si avrebbe avuto senza effettuare alcuna misura.

Per verificare l'importanza di questo fenomeno e valutare la qualità dei risultati ottenuti, i valori di concentrazione ottenuti dopo 88 ore di esposizione senza effettuare alcuna misura intermedia sono stati confrontati con i corrispettivi valori ottenuti effettuando due misure intermedie (dopo 20 ore e dopo 66 ore), depressurizzando il reattore ed esponendo i campioni all'aria durante la misura. I risultati di tale confronto sono riportati in tabella VI.1.

Tabella VI.1: confronto tra le frazioni massiche dopo 88 ore di esposizione, misurate effettuando due pesate intermedie e senza effettuare alcuna pesata intermedia.

Pressione, bar	Tipo di campione	**Frazione massica di CO_2 dopo 88 ore, %**		
		Senza misure intermedie		Con misure intermedie
		Valore medio	Intervallo sperimentale	
3	Bitume modificato	0.891%	0.819% - 0.931%	0.856%
	Bitume classico	0.412%	0.410% - 0.413%	0.398%
	Conglomerato	0.093%	0.088% - 0.095%	0.090%
9	Bitume modificato	1.709%	1.617% - 1.777%	1.662%
	Bitume classico	1.177%	1.168% - 1.193%	1.159%
	Conglomerato	0.113%	0.108% - 0.118%	0.107%

Come è possibile vedere dalla tabella, i valori di uptake ottenuti effettuato due pesate intermedie sono sempre inferiori rispetto ai corrispettivi valori ottenuti effettuando il processo senza alcuna interruzione. Questo dettaglio suggerisce la presenza di un fenomeno di rilascio di CO_2 durante il processo di misura che non è trascurabile. Ciononostante, molti dei valori ottenuti cadono all'interno dell'intervallo sperimentale, pertanto il fenomeno di rilascio di CO_2, sebbene presente, è relativamente limitato ed ha un effetto sui risultati comparabile a quello della variabilità sperimentale. Ciò significa che questo procedimento influenza la variabilità sperimentale con un errore dello stesso ordine di grandezza dell'errore sperimentale, confermando la qualità dei risultati.

Come nella prima fase realizzata a pressione atmosferica, anche in questa fase i dati sperimentali sono stati utilizzati per costruire un modello che permetta di predire la capacità massima di solubilizzazione e la cinetica del processo di solubilizzazione dei materiali in esame. Il modello selezionato è ancora una volta il modello di Peleg [42]. I risultati del modello e i relativi parametri sono presentati nella tabella VI.2.

Il primo elemento che può essere discusso è la massima capacità di solubilizzazione rappresentata dal parametro x_e. Nel caso del bitume modificato, per entrambe le pressioni, il valore è sensibilmente maggiore rispetto al valore misurato dopo l'esposizione di 88 ore. Secondo questo modello, il bitume modificato non raggiunge dei valori di concentrazione prossimi alla capacità massima dopo sole 88 ore di esposizione. Ciò è evidente anche osservando il parametro k, che rappresenta la velocità con cui la curva cresce. Per entrambe le pressioni (e anche nel caso a temperatura ambiente della fase precedente) k è dell'ordine di qualche unità, relativamente piccolo se comparato ai corrispettivi valori del bitume classico e del conglomerato. Sebbene il bitume modificato presenti una capacità massima di solubilizzazione maggiore rispetto al bitume classico, esso presenta una cinetica di solubilizzazione più lenta. Questo significa che questa formulazione impiega più tempo per raggiungere la capacità massima. Graficamente ciò si traduce in una curva che cresce più lentamente rispetto alla curva associata al bitume classico.

Tabella VI.2: Parametri del modello di Peleg per i tre materiali investigati a 3 e 9 bar.

Pressione, bar	**Tipo di campioni**	**k, h^{-1}**	x_e
3	Modificato	8.299	0.98%
	Classico	31.086	0.42%
	Conglomerato	502.728	0.092%
9	Modificato	4.379	1.88%
	Classico	10.905	1.25%
	Conglomerato	545.949	0.11%

Nel caso del bitume classico, la capacità massima calcolata con il modello è maggiore rispetto al valore misurato dopo 88 ore di esposizione. È possibile anche osservare come la costante cinetica associata al processo a 3 bar sia circa tre volte maggiore rispetto alla costante cinetica del processo realizzato a 9 bar. (E la costante cinetica del processo a pressione atmosferica, descritto nella fase precedente, è circa tre volte maggiore della costante a 3 bar). Nonostante la concentrazione massica di CO_2 aumenti linearmente con l'aumento della pressione, la cinetica del processo di solubilizzazione diminuisce progressivamente e la curva cresce più lentamente a pressioni più elevate. Se nel caso a pressione atmosferica l'uptake raggiunto dopo 88 ore di esposizione è prossimo alla capacità massima, nel caso a 9 bar c'è ancora un divario considerevole tra l'uptake raggiunto e la capacità massima calcolata.

Infine, il processo di solubilizzazione da parte del conglomerato bituminoso è quello con la cinetica più elevata, in quanto il parametro k è dell'ordine delle centinaia per entrambe le pressioni.

Come nella prima fase di questo studio, dopo aver concluso la caratterizzazione del processo di solubilizzazione di ciascun materiale, i campioni sono stati esposti all'aria a temperatura e pressione ambiente, per caratterizzare il processo di rilascio di CO_2 da parte dei campioni carbonati. Tutti i campioni esposti all'aria libera sono stati pesati progressivamente, in modo tale da misurare l'evoluzione della loro perdita di massa, direttamente legata all'anidride carbonica rilasciata. Lo scopo principale di questa parte dello studio è di caratterizzare la quantità minima di equilibrio. La definizione di questo parametro è importante per giudicare se questi materiali possono essere considerati dei candidati validi per lo stoccaggio permanente di anidride carbonica. In questa fase è stata caratterizzata anche la cinetica del processo di rilascio, ossia il tempo necessario affinché i campioni carbonati arrivino all'equilibrio termodinamico.

I risultati per le due formulazioni di bitume sono riassunti nella tabella VI.3, dove sono ordinati in base alla pressione utilizzata nel processo di carbonatazione. Nella terza colonna della tabella è indicata la concentrazione massica percentuale media in CO_2 dei campioni dopo 88 ore di esposizione nella cella di carbonatazione, mentre nella quarta colonna la concentrazione massica media dopo che gli stessi campioni sono estratti dalla cella ed esposti all'aria per 160 ore. Nella quinta colonna è possibile leggere la frazione di CO_2 media trattenuta da tali campioni, espressa come percentuale del valore all'inizio del processo di rilascio.

Tabella VI.3: Risultati del processo di rilascio di CO_2 in seguito all'esposizione dei campioni all'aria a condizioni ambiente

Tipo di campione	**Pressione del processo di carbonatazione, bar**	**Frazione di CO_2 media dopo 88 ore di carbonatazione, %**	**Frazione di CO_2 media dopo 160 ore di esposizione all'aria, %**	**Frazione di CO_2 trattenuta, %**
Bitume modificato	0 (pressione ambiente)	0.43%	0.35%	80.9%
	1.5	0.75%	0.46%	60.1%
	3	0.89%	0.52%	58.9%
	5	1.22%	0.49%	40.3%
	7	1.49%	0.52%	34.6%
	9	1.71%	0.56%	32.5%
	20	2.16%	0.48%	22.2%
Bitume classico	0 (pressione ambiente)	0.11%	0.04%	32.2%
	1.5	0.28%	0.01%	4.2%
	3	0.41%	0.05%	12.4%
	5	0.69%	0.07%	9.9%
	7	0.93%	0.05%	5.4%
	9	1.18%	0.06%	4.3%
	20	2.34%	0.08%	3.4%

Per entrambe le formulazioni di bitume, è possibile notare che, anche se la quantità di CO_2 inizialmente immagazzinata in seguito al processo di solubilizzazione aumenti all'aumentare della pressione all'interno della cella di carbonatazione, il valore finale dopo 160 ore di esposizione all'aria è circa costante, intorno allo 0.5% nel caso del bitume modificato, e nell'intervallo 0.05%-0.08% nel caso del bitume classico. Questo significa che la frazione di CO_2 trattenuta dal campione rispetto al valore inizialmente solubilizzato diminuisce all'aumentare della pressione.

Questo risultato è abbastanza interessante in quanto mostra che non è interessante utilizzare pressioni elevate all'interno della cella di carbonatazione con lo scopo solubilizzare permanentemente delle quantità di CO_2 più elevate, in quanto la quantità d'equilibrio naturalmente trattenuta dopo l'esposizione all'aria è relativamente costante e indipendente dalla pressione di carbonatazione applicata.

Tra i vari dati presentati in tabella VI.3, i valori relativi alla carbonatazione a 1.5 bar di pressione sembrano non seguire l'andamento degli altri risultati, in quanto per entrambe le formulazioni di bitume i campioni hanno rilasciato una quantità sensibilmente superiore di CO_2. Questa discrepanza può essere spiegata considerando che non tutti parametri sperimentali sono sotto controllo diretto durante gli esperimenti. In particolare, non è stato possibile controllare la temperatura del locale in cui le esperienze sono state realizzate, ed un ipotetico aumento locale di temperatura potrebbe aver accelerato il processo di rilascio di CO_2 e portato i campioni a trattenere quantità inferiori.

Per quanto riguarda il fenomeno di rilascio/desorbimento associato al conglomerato bituminoso, anche in questo caso la caratterizzazione è avvenuta mediante misura progressiva della massa dei campioni. Nelle figure VI.6 e VI.7 è possibile osservare la variazione dell'uptake massico percentuale del conglomerato bituminoso in funzione del tempo trascorso a partire dall'estrazione dei campioni dalla cella sperimentale, rispettivamente per una pressione di carbonatazione di 7 bar e di 9 bar. La cinetica di rilascio/desorbimento è molto elevata, e per tutte e tre i casi i campioni perdono l'intera quantità di CO_2 precedentemente trattenuta nel giro di poche ore.

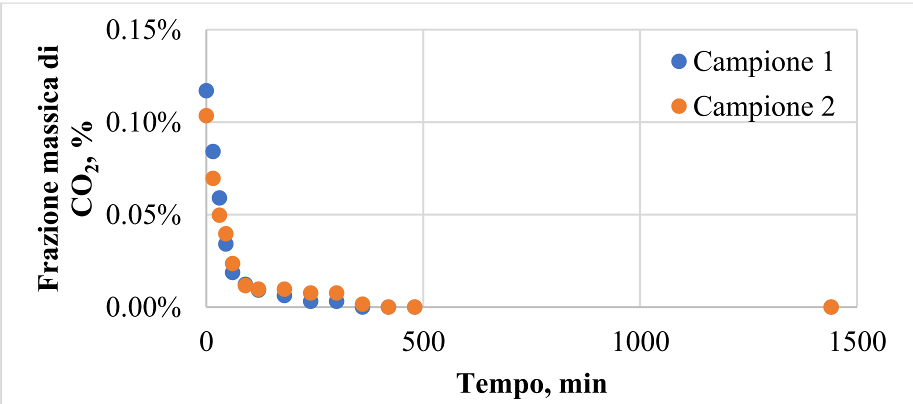


Figura VI.6: Frazione massica di CO_2 del conglomerato bituminoso sottoposto ad una pressione di carbonatazione di 7 bar, durante l'esposizione all'aria in condizioni ambiente.

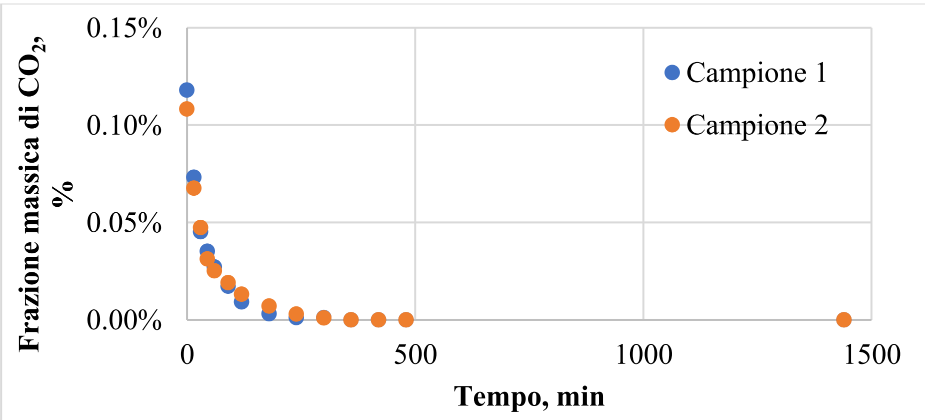


Figura VI.7: Frazione massica di CO_2 del conglomerato bituminoso sottoposto ad una pressione di carbonatazione di 9 bar, durante l'esposizione all'aria in condizioni ambiente.

Questo elemento suggerisce che il fenomeno alla base del processo di solubilizzazione della CO_2 in questo materiale è, almeno in parte, diverso da quello alla base della solubilizzazione nelle formulazioni di bitume. Nel caso del conglomerato bituminoso il processo è completamente reversibile in quanto tutta la CO_2 catturata viene rilasciata una volta che il campione viene esposto all'aria libera. Il fenomeno fisico che interviene potrebbe essere quindi un fenomeno di adsorbimento che interessa la componente solida granulare inerte del conglomerato, e che implica la formazione di deboli legami fisici tra il gas e la superficie del solido. Nel caso del bitume invece, la presenza di quantità di CO_2 residue anche dopo diversi giorni di esposizione all'aria libera potrebbe suggerire la formazione di legami chimici permanenti, soprattutto nel caso del bitume modificato, per il quale la quantità di CO_2 conservata è abbastanza importante, e per il quale l'aggiunta di additivi nella composizione della formulazione interviene sicuramente nella formazione di tali legami.

VII. Risultati della terza fase sperimentale

Il programma di temperatura utilizzato per l'analisi di GC presenta le seguenti caratteristiche:

- Temperatura costante di 45°C per 7.5 minuti
- Gradiente di temperatura di 45°C/min fino al raggiungimento di 260°C
- Temperatura costante di 260°C per 20 minuti

Tale programma è basato sul programma descritto da Sutter et Al. [51] (nel cui studio la cromatografia in fase gassosa viene utilizzata per la caratterizzazione dei fumi di bitume) ed è stato riadattato in funzione delle caratteristiche tecniche del cromatografo e della strumentazione a disposizione.

Per poter identificare i componenti rilasciati in seguito al riscaldamento delle formulazioni di bitume, il medesimo programma di temperatura è stato applicato prima di tutto ad una soluzione standard di alcani C_8-C_{20}, in modo da ottenere un cromatogramma di riferimento con cui identificare i componenti delle formulazioni di bitume.

Questo programma di temperatura è stato poi usato per la caratterizzazione dei fumi ottenuti dal riscaldamento di entrambe le formulazioni di bitume (bitume classico e bitume modificato) a temperature progressivamente crescenti (80°C, 100 °C, 120 °C, 140°C e 160°C).

I risultati dell'analisi per entrambe le formulazioni di bitume sono riassunti in tabella VII.1, in cui è possibile leggere il numero totale di picchi rilevati ad ogni temperatura di esposizione. L'analisi dei fumi prodotti dal riscaldamento del bitume modificato a 80 °C mostra la presenza di 38 picchi distinti, invece, se il bitume è riscaldato a 160°C, la GC rileva fino a 80 picchi. Nel caso del bitume classico, vengono rilevati 39 picchi distinti a 60°C e 76 picchi quando il campione è riscaldato a 160°C.

Osservando i risultati, è evidente come un aumento della temperatura porti al rilascio di un numero superiore di componenti volatili da parte dei campioni di bitume.

Non è stato possibile osservare delle differenze sostanziali in termini di numero di picchi tra le due formulazioni di bitume. Ciononostante, è stato possibile notare come nel caso del bitume classico i cromatogrammi presentino più picchi associabili agli alcani C_8-C_{20} rispetto ai cromatogrammi del bitume modificato. Le modifiche apportate alla formulazione di bitume potrebbero essere la causa della stabilizzazione di questi componenti, che vengono quindi rilasciati con più difficoltà rispetto al bitume classico a parità di temperatura di esposizione.

Altri picchi non associabili agli alcani C_8-C_{20} sono stati osservati per entrambe le formulazioni. La presenza di tali picchi sottolinea la necessità di ulteriori investigazioni in merito.

Tabella VII.1: Numero di picchi e relativi alcani identificati in seguito all'analisi GC dei fumi ottenuti riscaldando le due formulazioni di bitume a temperature crescenti. In **rosso** gli alcani per cui sono stati osservati picchi di intensità più elevata.

Temperatura, °C	Bitume modificato		Bitume classico	
	Alcani identificati	**N° di picchi**	**Alcani identificati**	**N° di picchi**
80	**C_{10}**, C_8, C_{11}, C_{14}, C_{18}	38	**C_{10}**, C_8, C_9, C_{11}, C_{12}, C_{14}, C_{18}	39
100	**C_{10}**, **C_{11}**, C_8, C_9, C_{13}, C_{18}	57	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{14}, C_{18}	53
120	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	62	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	59
140	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	63	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	67
160	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{17}, C_{18}	80	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{15}, C_{17}, C_{18}	76

VIII. Conclusioni

I risultati più interessanti di questo lavoro sono quelli relativi al bitume modificato. È stato infatti possibile verificare che in questa formulazione di bitume è possibile solubilizzare una quantità di CO_2 sensibilmente maggiore rispetto alla formulazione classica. La capacità di ritenzione di CO_2 del bitume modificato è circa quattro volte superiore rispetto al bitume classico quando i campioni vengono esposti ad una atmosfera di CO_2 a pressione ambiente. Se i campioni sono esposti a pressioni superiori, la differenza tra le capacità di ritenzione delle due formulazioni si riduce, ma il bitume modificato rimane in ogni caso il materiale che può solubilizzare la quantità maggiore di anidride carbonica.

Il bitume modificato può inoltre trattenere una quantità non trascurabile di CO_2 anche dopo oltre 9 giorni di esposizione all'aria libera a pressione e temperatura ambiente. Si tratta in media di una quantità dello 0.5%, espressa in frazione massica percentuale, che può essere confrontata con la frazione massica di CO_2 naturalmente presente nell'aria, che è intorno allo 0.063%. Tale quantità è indipendente dalla pressione utilizzata nel processo di carbonatazione. Il fatto che questo materiale trattenga una tale quantità di anidride carbonica anche dopo un'esposizione relativamente lunga all'aria, indica che le interazioni alla base del processo di solubilizzazione sono basate su legami relativamente forti, che conferiscono al sistema bitume-CO_2 una certa stabilità a condizioni ambiente. Il bitume modificato è stato oggetto di diverse modifiche che ne hanno variato la composizione chimica mediante l'aggiunta di additivi, i quali evidentemente promuovono la formazione di interazioni forti e migliorano la stabilità del prodotto carbonato.

Anche il bitume classico trattiene una certa quantità di CO_2 dopo 9 giorni di esposizione all'aria libera, ma si tratta di una quantità decisamente inferiore (tra lo 0.05% e lo 0.07% in frazione massica), che anche in questo caso non dipende dalla pressione utilizzata nel processo di carbonatazione.

La cinetica del processo di solubilizzazione, sia a pressione atmosferica, sia a pressioni superiori, è più lenta nel caso del bitume modificato e più veloce nel caso del bitume classico. Per il bitume modificato inoltre, l'aumento della pressione (nell'intervallo 1-10 bar) non sembra avere effetti importanti sulla cinetica del processo di solubilizzazione, in quanto la costante cinetica del modello realizzato a partire dai risultati sperimentali è sempre dell'ordine di qualche unità, indipendentemente dalla pressione utilizzata.

Il bitume classico presenta una cinetica molto più veloce. I campioni di questa formulazione raggiungono valori prossimi alla capacità massima calcolata in pochi giorni, soprattutto nell'esperienze effettuate a pressione atmosferica. Se la pressione aumenta, il bitume classico presenta una capacità di solubilizzazione maggiore (che cresce linearmente con la pressione), ma la cinetica del processo rallenta. La costante cinetica del modello empirico applicato infatti ha un valore di circa 90 h^{-1} a pressione ambiente, circa 30 h^{-1} a 3 bar di pressione e intorno a 10 h^{-1} a 9 bar di pressione. Pertanto, sebbene sia possibile solubilizzare quantità di CO_2 superiori nel bitume classico semplicemente aumentando la pressione, per raggiungere la capacità massima di equilibrio è necessario attendere tempi progressivamente maggiori.

Il conglomerato bituminoso invece, presenta una capacità di ritenzione di CO_2 molto bassa se la carbonatazione è effettuata a pressione ambiente. Se la carbonatazione avviene a pressioni più importanti, questo materiale può assorbire quantità di CO_2 non trascurabili (0.1%

in massa a 9 bar di pressione). Ciononostante, quando il conglomerato è esposto all'aria libera, perde tutta la CO_2 precedentemente solubilizzata nel giro di poche ore.

I risultati dell'analisi cromatografica hanno permesso di caratterizzare parzialmente la composizione dei fumi prodotti in seguito al riscaldamento di entrambe le formulazioni di bitume a temperature fino a 160°C. L'aumento di temperatura porta al rilascio di un numero superiore di componenti volatili. L'analisi realizzata ha permesso di identificare composti associabili agli alcani C_8-C_{20}, ma la presenza di altri picchi suggerisce l'esistenza di altri componenti non ancora identificati.

Summary

1. Introduction

In this work, the CO_2 solubilization phenomenon in different bitumen formulations is studied, including pure bitumen. The purpose of this work is not only to evaluate the retained CO_2 quantities in bitumen formulations at ambient temperature and pressure, but also to assess how these quantities change by varying the system temperature and pressure.

The desired results are, in the first place, the maximal CO_2 capacity for each formulation at given temperature and pressure, but also the evolution over time of the dissolved CO_2 quantity, which will allow to characterize the dissolution process kinetics. With the same principle, by leaving the carbonated sample in contact with air in ambient conditions, an evaluation of the released CO_2 quantity over time allows to characterize the CO_2 release kinetics.

The main objectives of this work are the quantification of the retained CO_2 in bitumen and in other bituminous materials (Recycled Asphalt Pavements) through a rigorous experimental procedure and the characterization of the real nature of the CO_2 diffusion mechanism in these materials.

The presented work has been organized in three different experimental steps.

In the first step of the work, the CO_2-bitumen and CO_2-RAP systems are investigated under ambient temperature and pressure ($\simeq$ 20 °C, $\simeq$ 1 bar absolute), to quantify the maximal CO_2 capacity and the sorption and desorption kinetics under these conditions. During this first group of experiences, the natural CO_2 retention potential of these materials has been characterized. The analysis has been carried out by following a simple experimental procedure in which the samples are placed in a cylindric cell which is subjected to a constant CO_2 flowrate. The CO_2 mass flow rate through the cell is controlled by means of a flowmeter. Another flowmeter is placed at the exit of the cell: in principle the amount of CO_2 retained in the sample can be characterized in two ways: by observing the mass variation of the samples and by analyzing the difference between the two mass flows. However, for these materials the dissolved CO_2 quantities are relatively small, so that the amount of absorbed CO_2 over time cannot be appreciated using the flowrate difference experimental procedure. Because of this, gravimetric analysis is the principal experimental procedure utilized in this part of the work to characterize the solubilization process in terms of both maximum capacity and kinetics. Then, by exposing the sample to free air, it has been also possible to measure the amount of CO_2 released progressively.

In the second part of the work, the process of CO_2 solubilization in the investigated materials has been carried out at pressures different from ambient conditions. Experimental campaigns have been carried out at pressures above ambient pressure and at ambient temperature (about 20 °C). Experimental pressures up to 20 bar were utilized, in line with the construction limits of the equipment. The analyses have been carried out more in detail for the 1-10 bar pressure window, for which there are almost no experimental results in literature, where a comprehensive characterization of the process of solubilization has been made using experimental data relating to pressures starting from at least 2 Mpa (20 bar) and generally for several tens of bars (up to more than 10 Mpa, 100 bar), but very little information is available for lower pressures, which have been employed in this work. The long overall duration of each experiment allowed to characterize the maximum CO_2 solubilization capacity in the analyzed materials only for certain pressures, but in any case, it has been possible to define the absorbed quantities after a certain period (some days), and how this quantity varies with the pressure of the experimental system. It has also been possible to characterize the solubilization kinetics (already defined in the ambient pressure experiment), for higher pressure conditions.

As in the previous phase, the carbonated samples have been exposed to the free atmosphere, progressively monitoring the mass of CO_2 released and thus making it possible to assess whether and how the amount of CO_2 in the carbonate samples changes over time when they are exposed to the atmosphere, depending on the solubilization pressure previously applied and, therefore, on the fraction of CO_2 initially solubilized.

The purpose of this second step of the work is to try to assess if the pressure parameter can be used to maximize the maximum amount of CO_2 that can be solubilized in the materials under investigation, and define how the CO_2 solubilized amounts vary after several days of exposure to free air at room conditions, in order to try to understand how to retain higher quantities.

In the third and last step, the experimental system was subjected to temperatures above room temperature. In this step of the work, the components that are naturally released when the samples are subjected to temperatures up to 160°C are characterized. This characterization is qualitative, by means of gas phase chromatography analysis. The purpose of this third step of the work is to define qualitatively whether a temperature increase leads to a more significant release of volatile components, and to verify whether the spectrograms of the different samples investigated in this study show any differences at different temperatures up to 160 °C, and whether these differences can be attributed to the different composition of the materials. A diagram presenting the three experimental steps that have characterized this work is presented in Figure 1.1.

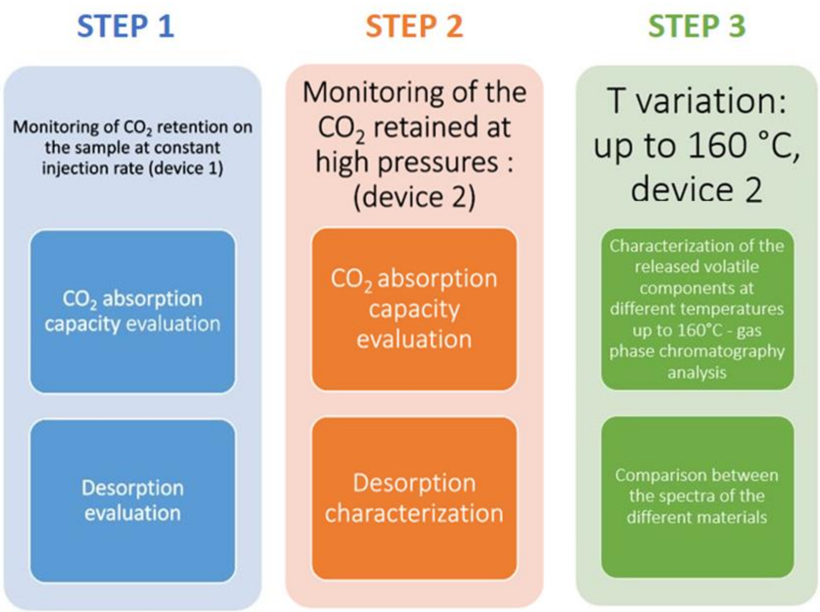


Figure 1.1: Experimental steps

2. Bibliographic research

2.1. Context and definitions

2.1.1. Bitumen composition and characteristics

In recent years, a whole range of energy geopolitics events and technological development has increased the interest in heavy oil residues (heavy oil, bitumen) with the aim of processing them, to obtain gasoline and other liquid fuels. To optimally exploit these heavy petroleum fractions, an in-depth understanding of their chemical composition and chemical-physical properties has proved to be indispensable.

Generally, the petroleum feedstocks are quite complex in terms of chemical composition, they consist of 10^5 to 10^6 different molecules [60]. Because of this, a chemical characterization of the entire feedstock would be impossible, nevertheless it is possible to operate a delineation of the different components by separation of the products in different phases, with different techniques (solubility/insolubility in solvents, adsorption/desorption, distillation) [60].

The most common method used in the petroleum industry for separation of heavy oil fractions such as bitumen into different classes of compounds, is SARA analysis (Saturates, Aromatics, Resins, Asphaltenes) which allows to separate the components of heavy oil fractions into four broad chemical groups with the following characteristics [21]:

- Saturates: molecular weight in the range 500-800, solids or viscous liquids.
- Aromatics: Molecular weight typically in the range 500-900, dark brown viscous liquids.
- Resins: Molecular weight in the 900-1300 range, dark brown solids, or semi-solids, soluble in paraffinic solvents, adhesive and polar.
- Asphaltenes: high molecular weight 1000 – 50000, brown/black amorphous solids or semi-solids, generally precipitated from bitumen by dissolving it in a paraffinic solvent.

The Resins, Aromatics and Saturates fractions are often grouped in a single fraction known as Maltenes**.** A quite simple depiction of the bitumen composition can be visualized in Figure 2.1, which represents a colloidal system in which the Asphaltenes are dispersed in the lower molecular weight Maltenes under a “micelles” structure [40]: the Asphaltenes molecules are stabilized by different layers of components mostly in the Resins fraction, constituting some micelles-like structures, dispersed in a medium of Aromatics and Saturates components.

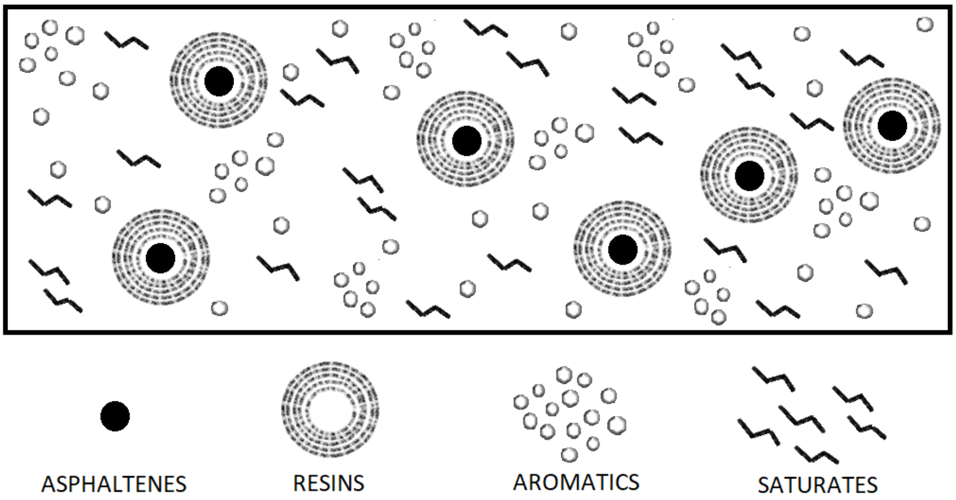


Figure 2.1: The colloidal composition of bitumen, modified from Nicholls [40].

Typical SARA technique results for Cold Lake and Athabasca bitumen are shown in Table 2.1. In the table there are the molar weight of the principal bitumen components and the percentage mass fraction in terms of components and in terms of elements for different types of bitumen formulations. Bitumen is predominantly composed of hydrocarbons molecules, with a small quantity of heteroatom-containing components, most of which contain Nitrogen, oxygen, or sulfur. However, bitumen also contains traces of metallic species (nickel, iron, vanadium, etc.) [43]. Harder bitumen can be produced from soft penetration bitumen by subjecting it to high temperatures and/or vacuum conditions: in such a way the more volatile components (aromatics fractions and saturates) are removed, concentrating the Asphaltenes and resins [21].

Generally, at environment temperatures bitumen is stable and inert, but if it is exposed to the atmosphere in very thin films, an oxidation process can occur, slowly hardening the bitumen, until it becomes brittle [21]. This oxidation process increases the resins and asphaltenes fraction, producing on the bitumen sample the same chemical changes than happen when it is exposed to high temperatures: a molecular weight increase and sample hardening.

Usually, the bitumen physical properties that are characterized are those related to its performance as road binder, namely its rheological properties and its mechanical strength. In relation to the latest extraction techniques involving the decrease of the viscosity of bitumen by means of different techniques, including temperature increase or injection of different gases (i.e., CO_2), the variations in the rheological properties of bitumen as a function of these parameters are increasingly being studied.

Table 2.1: Properties and SARA fractionation results for Athabasca and Cold Lake bitumen, modified from Rahimi et Al., 2007 [43].

	Athabasca		Athabasca	Cold Lake		Cold Lake
	Modified ASTM 2007		**ASTM 2007**	**Modified ASTM 2007**		**ASTM 2007**
	MW, g/mol	**Mass fraction, %**	**Mass fraction, %**	**MW, g/mol**	**Mass fraction, %**	**Mass fraction, %**
Saturates	381	17.27	16.9	378	20.74	21.52
Aromatics	408	39.7	18.3	424	39.2	23.17
Resin	947	25.75	44.8	825	24.81	39.36
Asphaltenes	2005	17.28	17.18	1599	15.25	15.95
Carbon		83.34			83.62	
Hydrogen		10.26			10.5	
Sulfur		4.64			4.56	
Oxygen		1.08			0.86	
Nitrogen		0.53			0.45	
Residue		0.15			0.01	

2.1.2. RAP (Reclaimed Asphalt Pavements) management and properties

The acronym RAP (*Reclaimed Asphalt Pavements or Recycled Asphalt Pavements*) indicates removed and/or reprocessed pavements materials containing asphalt and aggregates [54]. RAP are the result of the asphalt concrete recycling process (the asphalt concrete is a composite material that consists of mineral aggregates such as sand, gravel, slag, crushed stone, etc., bound together with bitumen, laid in layers, and compacted) [14][49].

Research has proved that RAP can theoretically replace the need for up to 100% of the aggregate and bitumen binder in the mix [47], but this percentage is lower due to regulatory laws. In 2019 new asphalt pavements produced in the US contained on average 21.1 % RAP [61].

The properties of RAP depend on the properties of the original materials, there can be important differences in asphalt mixes in terms of aggregate size, consistency, and quality. The typical ranges of values related to the physical and mechanical properties of Reclaimed Asphalt Pavements are reported in table 2.2.

Table 2.2: Physical and mechanical properties of reclaimed asphalt pavement, modified from [54].

Type of Property	RAP Property	Typical Range of Values
Physical Properties	Unit Weight	1940 - 2300 kg/m^3
		(120-140 lb/ft$^{3)}$
	Moisture Content	Normal: up to 5%
		Maximum: 7-8%
	Asphalt Content	Normal: 4.5-6%
		Maximum Range: 3-7%
	Asphalt Penetration	Normal: 10-80 at 25°C (77°F)
	Absolute Viscosity or Recovered Asphalt Cement	Normal: 4000 - 25000 poises at 60°C (140°F)
Mechanical Properties	Compacted Unit Weight	1600 - 2000 kg/m^3
		(100-125 lb/ft^3)
	California Bearing Ratio (CBR)	100% RAP: 20-25%
		40% RAP and 60% Natural Aggregate: 150% or higher

2.1.3. The interest of the CO_2-bitumen system

Enhanced Oil Recovery (EOR), also known as tertiary recovery, is a group of different techniques that allow to extract the crude oil from an oil field that could not be extracted otherwise. EOR techniques can extract up to 60 % of a reservoir's oil, compared to 20 – 40 % of primary and secondary recovery [55].

The most important techniques of EOR are thermal injection, chemical injection, and gas injection. For all these techniques, the final purpose is usually to reduce the viscosity of the crude oil to be extracted: these techniques are used in cases where the reservoirs contain heavy and viscous oils (including bitumen), whose extraction is not possible with conventional techniques. Nevertheless, these techniques are mainly used to exploit mature fields more efficiently: oil authorities are more and more concerned in increasing oil recovery from the aging resources. In addition, the rate of replacement of the produced reserves by new discovered ones has been declining in the last years [1]. EOR techniques have proved indispensable to meet current and future energy demand, by increasing the recovery factors of the reserves currently exploited.

Thermal injection consists in different methods used to heat the crude oil in the reservoir to reduce its surface tension, its viscosity and to increase its permeability. These methods include steam injection and fire flooding. Steam injection consists in introducing heat to the reservoir by pumping steam into the well. Fire flooding consist in generating heat by combustion: continuous injection of air in the well allows to maintain the flame front and to produce the heat that reduces the oil viscosity.

Chemical injection consists in the usage of some chemicals to reduce the oil's surface tension. Between these chemicals there are alkaline solutions, water-soluble polymers, micro-emulsions, surfactants.

Gas injection is the most common approach and consist in introducing soluble gases into the reservoir to improve oil mobility by reducing the interfacial tension between oil and water. Gases used include CO_2, natural gas, and nitrogen.

The United States has been using CO_2–EOR techniques in the last decades. CO_2 flooding from natural sources has been the most important EOR process in the US especially in carbonate reservoirs of the Permian Basin [1]. CO_2-EOR is expected to continue to grow, but if CO_2 flooding techniques are to be increasingly implemented, non-natural CO_2 sources will need to be exploited at competitive costs. Today the climate change topic is an issue of intense discussion, and CO_2-EOR has become an attractive CO_2 storage alternative among the options currently available: it is possible to benefit from carbon dioxide high potential in recovery of stranded heavy oils and bitumen sitting deep in depleted reservoirs as a Carbon dioxide Capture Utilization and Storage technique. An emission reduction strategy that combines CO_2 storage with EOR is today quite interesting because it allows to associate the costs related to the two single processes and to maximize the possible incomes (crude oil produced and carbon credits). Despite that, right now the costs of CO_2 capture, compression and transportation technologies are too high, making CO_2-EOR economically unattractive [1], if not implemented from natural resources. Nevertheless, the costs reduction associated with CO_2 capture and compression technologies, and a revaluation of carbon credits, would make this technological solution economically attractive.

Considering CO_2 emissions and environmental impact of bitumen (and heavy oil) transportation as major challenges in oil sand operation (Alberta), the high CO_2 dissolution capacity in bitumen has been pointed out as an important opportunity to propose a new approach that consists in using diluted bitumen as carrier for large-scale CO_2 transportation, to reduce the CO_2 transportation costs by utilizing the CO_2 Carbon Capture Utilization and Storage value chain. These opportunities offer the possibility of sustaining access to oil resources while reducing environmental impact and improving the economics of CCUS and oil sands operations. It has been proved that 80–200 kg of CO_2 per m^3 of bitumen can be dissolved and transported [64].

When injected into the reservoir, carbon dioxide diffuses into the oil, causing a reduction in its viscosity. At this point the oil can be drained into the production well to be pumped out. The most significant parameters in the CO_2-EOR process are temperature, pressure of the reservoir, amount of dissolved CO_2 and shear rate applied to the bitumen. The effect of these parameters on the viscosity reduction has been the subject of a lot of studies that have tried to characterize the viscous behavior of the CO_2-heavy oil/bitumen systems.

Considering that the CO_2-bitumen thermodynamic system is of considerable importance in relation to EOR CO_2-injection techniques, it is not surprising that in the scientific literature many studies have characterized the thermodynamic and rheological characteristics of this system. Many of these studies focused on the measurement and modelling of the viscosity of bitumen/heavy oil and how this property varies according to the parameters mentioned above, especially the amount of dissolved CO_2. Some of these studies and their experimental conditions are given in Table 2.3.

Table 2.3: Selected studies on viscosity measurement of heavy oils and bitumen in the presence of CO_2.

Author	System	Temperature, °C	Pressure, Mpa	Viscometer
Simon and Graue [48]	CO_2-saturated crude oils	43.3-121.1	15.6	Zeitfuchs cross-arm for the atmospheric–pressure viscosity and a rolling-ball viscometer for the high pressure viscometry
Jacobs et al. [22][23]	CO_2-saturated Athabasca bitumen	20-140	5.7	In-line Contraves Model DC 44 viscometer coupled with a magnetic cup
Svrcek and Mehrotra [52]	CO_2-saturated Athabasca bitumen	25-100	6	In-line Contraves Model DC 44 viscometer coupled with a magnetic cup
Mehrotra and Svrcek [31]	CO_2-saturated Marguerite Lake bitumen	12-103	7	In-line Contraves Model DC 44 viscometer coupled with a magnetic cup
Miller and Jones [39]	CO_2-saturated Wilmington and Cat Canyon heavy oils	24, 60 and 93	34.5	Rolling-ball
Jha [25]	CO_2-saturated reservoir fluids and wellhead heavy oil	28	8.3	Pressure drop (capillary)
Mehrotra and Svrcek [35]	CO_2-saturated Cold Lake bitumen	15-97.9	11	In-line Contraves Model DC 44 viscometer coupled with a magnetic cup
Chung et al. [8]	CO_2-saturated Bartlett heavy oil	24, 60 and 94	34.5	Rolling-ball
Sayegh et al. [45]	CO_2-Lindbergh saturated heavy oils	21 and 140	15	Pressure drop (capillary)
Kokal and Sayegh [27]	CO_2-Lone Rock saturated heavy oils	21 and 140	12.4	Pressure drop (capillary)
Badamchi-Zadeh et al. [3]	CO_2-C_3H_8-Athabasca bitumen	0 - 90	5	ViscoPro2000 Cambridge viscometer limited to 6.9 MPa and 190 °C

Behzadfar work [6] has analyzed the effects of temperature, pressure, and amount of dissolved CO_2 on the bitumen rheology, measuring its viscosity in a temperature range between -10°C and 180 °C and at pressures up to 15 MPa. This study also modeled the effects of these parameters on the viscosity of bitumen by utilizing a reduced variable method.

The effect of temperature on bitumen viscosity that has been observed in Behzadfar study [6] is quite predictable and intuitive: an increase in temperature leads to a decrease in viscosity and their correlation is effectively described with a double-log law.

The influence of pressure is not as profound as that of temperature, as the pressure increases the bitumen viscosity slightly increases. The pressure effect is weaker when the temperature is higher.

The results about the dissolved CO_2 effect on bitumen rheology show why this gas is used to reduce the bitumen viscosity and raise the production rate in EOR. Carbon dioxide is one of the most effective gases because of its high solubility in heavy oils and bitumen. As the saturation pressure increases, the bitumen viscosity decreases, and this effect is stronger at lower temperatures.

2.1.4. Distinction between adsorption and absorption phenomena

To study the thermodynamic, kinetic, and rheological characteristics of the CO_2-bitumen system or CO_2-RAP system, it is first necessary to characterize the type of interactions that occur between the carbon dioxide and the materials in question. Since both bitumen and Reclaimed Asphalt Pavements are substances have a very complex composition, and quite difficult to characterize, it is also difficult to define precisely the nature of the interactions that occur when carbon dioxide comes into contact with these materials. Nevertheless, a first element of investigation consists in making a distinction between two physical-chemical phenomena that generally intervene in the processes that involve the solubilization of a gas in a medium: these two phenomena are adsorption and absorption. A scheme of the mechanisms of the two phenomena is shown in Figure 2.2.

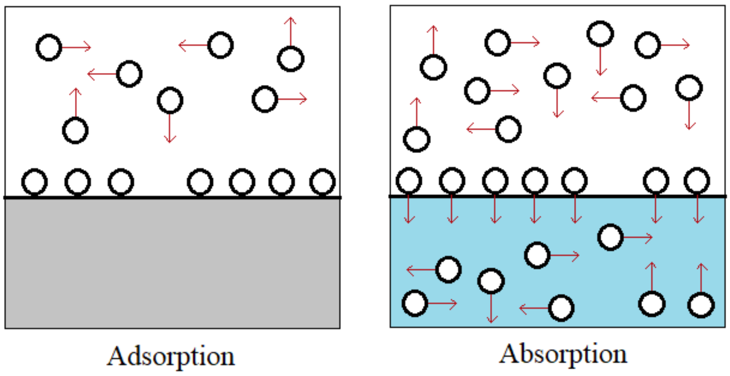


Figure 2.2: Schematic representation of adsorption and absorption processes.

Adsorption is defined as “the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface” [30]. This process creates a film of the adsorbate on the surface of the adsorbent. The adsorption is a surface phenomenon and the surface where the process takes place is called interface. The exact nature of the bonding depends on the characteristics of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding).

On the other hand, absorption can be defined as “a physical or chemical phenomenon in which atoms, molecules or ions enter some bulk phase – liquid or solid material”, in this sense, the molecules undergoing absorption are taken up by the volume and not by the surface, because of that absorption is a bulk phenomenon [30]. Absorption is a process that may be chemical (reactive) or physical (non-reactive). Being a bulk phenomenon, absorption implies diffusion of one species into the other one.

In relation to the systems that will be investigated in this work, in all the sources analyzed for this first bibliographical phase, the interaction between bitumen and carbon dioxide is always described as a process of absorption, dissolution or diffusion, all terms that suggest that CO_2 interacts actively with the entire volume of bitumen and thus excluding the hypothesis of a purely superficial process. This observation is intuitive when it is considered that bitumen is a fluid and viscous material, rheologically and structurally distant from granular solid materials or powder with high surface area, which are generally the protagonists of adsorption processes. However, as regards the interaction between carbon dioxide and asphalt aggregates, no sources which analyze in detail the type of interaction that characterizes these two substances have been found. Nevertheless, considering the composite nature of RAP (mineral Aggregates bound together with bitumen) it can be assumed that the physical/chemical process involved is extended to the surface (in particular to the solid granular materials) and to the bulk, therefore it is possible to imagine that both phenomena intervene simultaneously: adsorption and absorption.

2.2. CO_2 solubility in bitumen

2.2.1. Overview

Most studies investigating the bitumen-CO_2 system aim at characterizing the process of gas injection (Enhanced Oil Recovery), in which carbon dioxide is injected into reservoirs in such a way that, diffusing in bitumen or heavy oils in general, it decreases its viscosity and facilitates its extraction. For this reason, many of the analyzed works, besides trying to study the rheological behavior of the system as a function of the various thermodynamic parameters, try to characterize the solubility of CO_2 in bitumen under thermodynamic equilibrium conditions, as a function of pressure and under different temperatures.

These studies use a relatively complex experimental setup to analyze the amount of CO_2 absorbed in each sample of bitumen once the thermodynamic equilibrium is reached, and how this quantity varies as a function of system pressure and temperature. Then the experimental data obtained are often used for the construction or verification of models (based on various types of equations of state) which effectively predict the evolution of solubility as a function of thermodynamic properties. Figure 2.3 shows the approach just described.

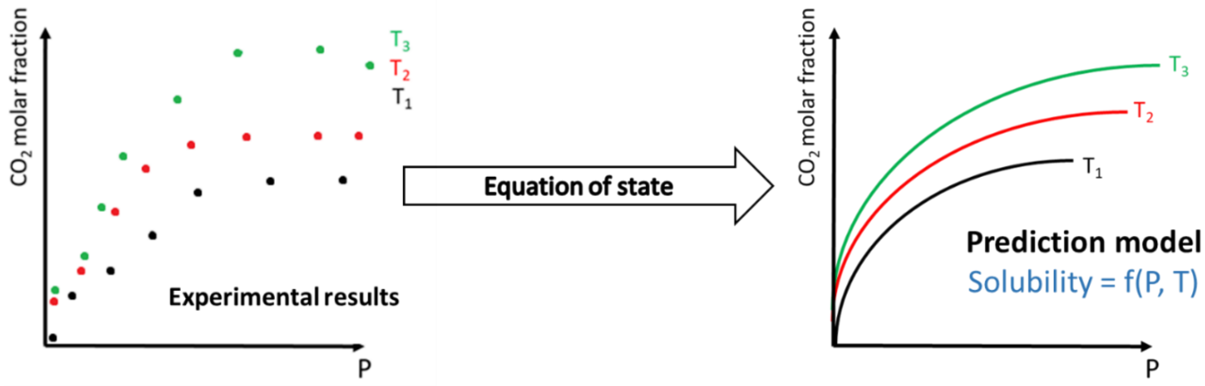


Figure 2.3: Description of the approach for the theoretical characterization carried out by the studies analyzing the CO_2 solubility in bitumen.

In Table 2.4 there is a list of studies that have characterized the solubility of CO_2 in bitumen. These studies are classified according to the type of bitumen used: as already stated, bitumen is a substance with a very complex and variable composition, two bitumen formulations of distinct origin may have very different physical, chemical, rheological, mechanical characteristics, etc., in this case in terms of the solubility of a gas. For this reason, it is necessary to carry out such classification to be able to correctly compare the various experimental data and results.

For each of the studies analyzed, several predictive models based on different state equations have been proposed. The equations of state utilized are the Cubic-Plus-Association Equation of State, Peng Robinson Equation of State, Schmidt-Wenzel Equation of State and Statistical Associating Fluid Theory.

For each predictive model the absolute average relative deviation percent value is reported. This parameter allows evaluating how much the proposed predictive model agrees with the experimental data collected. The smaller AARD% is, the better the model predicts the experimental results.

The AARD% is defined by Equation 2.1:

$$AARD\% = 100 \sum \left| \frac{x_{calc} - x_{exp}}{x_{exp}} \right| \tag{2.1}$$

Finally, for each study analyzed, the **temperature and pressure ranges** in which the experimental data were collected (and in which predictive models are valid) are reported.

Table 2.4: AARDs of the experimental data for CO_2 solubility in bitumen and the results of this model and other predictive models.

Type of Bitumen	Experimental Data	Predictive Models	AARD, %	Temperature Range, °C	Pressure Range, bar
Athabasca	Svrcek and Mehrotra [52]	Proposed model (CPA-EoS)	5.1	23 - 97.4	16 - 63.8
		Kariznovi et al. [26] (PR-EoS)	9.34		
		Mehrotra et al. [36] (PR-EoS)	7.6		
	Haddadnia et al. [52]	Zirrahi et al., [65] (PR-EoS)	4.3	70 - 190	20 - 80
	Deo, Wang and Hanson [13]	Deo et al. [12] (SW-EoS)	7.8	85 - 120	6.9 - 61.4
		Deo et al. [12] (PR-EoS)	7.65		
Cold Lake	Mehrotra and Svrcek [35]	Proposed model (CPA-EoS)	1.4	14.7 - 98.2	21.4 - 109.5
		Kariznovi et al. [26] (PR-EoS)	8.89		
		Eastick et al. [15] (PR-EoS)	6.8		
		Mehrotra and Svrcek [34] (PR-EoS)	1.9		
	Yu et al. [62]	Proposed model (CPA-EoS)	2.19	50 - 250	40 - 160.4
Peace River	Mehrotra and Svrcek [32]	Proposed model (CPA-EoS)	4.89	22.2 - 107	15 - 62.1
		Kariznovi et al. [26] (PR-EoS)	8.77		
		Mehrotra et al. [36] (PR-EoS)	9.3		
	Mehrotra et al. [38]	Proposed model (CPA-EoS)	8.32	79.5 - 202.75	20.8 - 99.5
		Mehrotra et al. [36] (PR-EoS)	7.7		
Wabasca	Mehrotra and Svrcek [33]	Proposed model (CPA-EoS)	5.43	21.4 - 150	14.6 - 66.2
		Kariznovi et al. [26] (PR-EoS)	8.8		
		Mehrotra et al. [37] (PR-EoS)	5.7		
Tar Sand Triangle	Deo, Wang and Hanson [13]	Deo et al. [12] (SW-EoS)	4.25	85 - 120	6.9 - 55.2
		Deo et al. [12] (PR-EoS)	4.1		
PR Spring	Deo, Wang and Hanson [13]	Deo et al. [12][35] (SW-EoS)	2.98	85 - 120	6.9 - 55.2
		Deo et al. [12][35] (PR-EoS)	3.01		

2.2.2. Experimental procedures

Most of the studies analyzed [17] [32] [33] [35] [38] [52] [62] utilize an experimental apparatus which, although it varies from work to work, functions based on the same operation principles and presents a set of elements common to all studies. These elements are:

- The equilibrium cell (or mixing cell) connected to at least two lines: one for the bitumen (re)circulation to help the gas absorption and to allow to reach equilibrium faster, and one for the CO_2 injection. This mixing cell is often equipped with different equipment to ensure the equilibrium achievement (mixing systems or systems that allows to increase the contact surface between bitumen and carbon dioxide).
- A pump to handle to bitumen in the circuit, considering the high viscosity of the material to be moved, volumetric pumps such as a gear pump are used.

- A sampling cell in which part of the saturated CO_2 bitumen present in the circuit is poured, once the achievement of equilibrium is assured, the content of the sampling cell can be extracted and analyzed.
- A viscometer, a densitometer, a flowmeter, or other equipment, depending on which properties are investigated.

Generally, this experimental set-up works according to this procedure: after the gas injection, the bitumen is recirculated until the investigated properties (viscosity, density of equilibrium pressure in the system) stabilizes, at which point the thermodynamic equilibrium is reached, the circulation is stopped, and the temperature, pressure, density, and viscosity of the mixture are recorded. Obviously, each study has an experimental set-up with different characteristics and a distinct operating procedure, but generally the description just presented summarizes quite well the elements in common with all experimental apparatuses.

Figure 2.4 shows an example of a generic experimental apparatus that could be used for the characterization of the bitumen-CO_2 system. This scheme is based on the characteristics shared by the different experimental setups described in the consulted studies [17][32][33][35][38] [52][62].

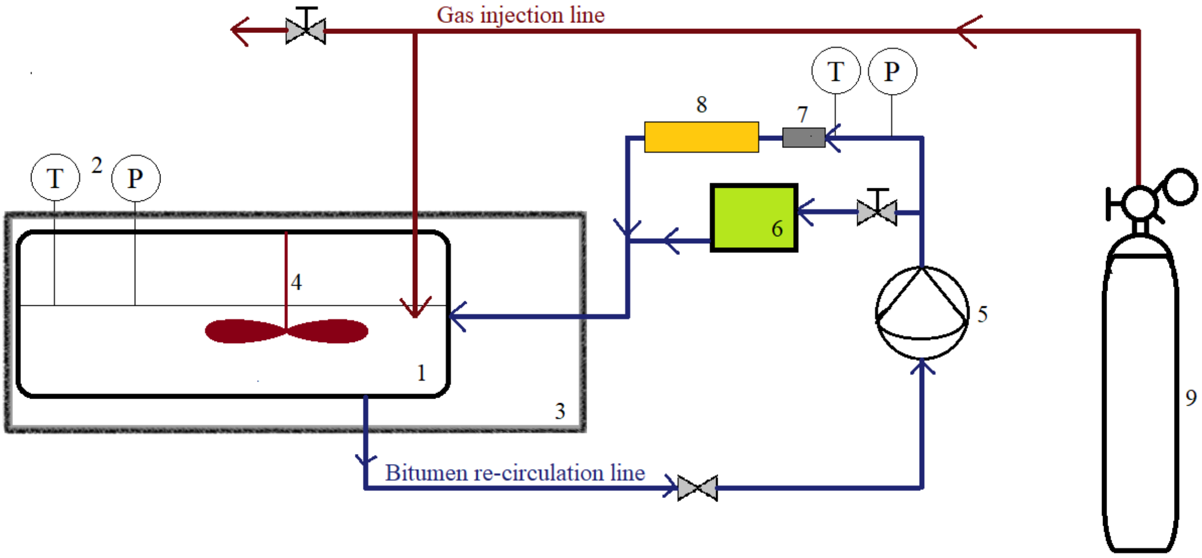


Figure 2.4: Example of a generic experimental setup used for the bitumen-CO_2 system characterization. 1:Equilibrium Cell; 2:Pressure/Temperature meters; 3:Oven; 4:Mixing system; 5:Volumetric Pump; 6:Sampling cell; 7:Filter; 8:Viscometer, densitometer, flowmeter, etc.; 9:CO_2 bottle.

Deo et Al. [13], instead of using an experimental system comparable to the one just presented, uses a high-pressure thermogravimetric analysis system. Thermogravimetric analysis (TGA) is a thermal analysis technique in which the sample mass is monitored over time as its temperature changes. This mass measurement provides information about a whole series of physical phenomena, such as sorption and phase transitions; in this study, the bitumen mass is measured over time, the CO_2 injection in the atmosphere above the sample causes a carbon dioxide diffusion in the bitumen volume, some of the CO_2 is absorbed and the mass of the sample increases. When the mass/time curve reaches a plateau, the thermodynamic equilibrium is considered achieved, and the properties of the sample are recorded.

2.2.3. Results

The first element that is easy to identify from the analysis of the results of these studies, is that the CO_2 solubility in bitumen increases with increasing pressure and decreases with increasing temperature. This trend is shared with the results of countless studies dealing with the solubility of other gases (CH_4, C_2H_6, C_3H_8, and N_2) in bitumen or other heavy oils. It can be stated as a rule that, irrespective of the type of dissolved gas, for gas-saturated bitumen an increase in temperature or a decrease in pressure usually results in a lower gas solubility.

The decrease in solubility at increasing temperature can be explained by considering that at higher temperatures the molecular mobility of the gas is higher, and therefore the gas has a lower tendency to remain absorbed in the bitumen volume. Evidently, the increase in solubility at increasing pressure is linked to an increasing amount of carbon dioxide in the atmosphere around the sample. It can also be observed that at lower temperatures, the effect of the pressure increase on solubility is accentuated (the curve grows faster).

In table 2.5 it is possible to observe the maximum solubility values observed for each type of bitumen, expressed in molar percentage and mass percentage, with the corresponding temperature and pressure conditions. It is possible to dissolve considerable amounts of CO_2 in bitumen, often up to 60 mol% (9-13 wt%), at temperatures close to room temperature, but at relatively high pressures (between 60 and 110 bar).

Generally, all the sources used in this bibliographical study analyze the bitumen-CO_2 system at relatively high pressures (dozens of bars, > 7 bars), this is because these studies analyze the thermodynamic bitumen-CO_2 system with the aim of characterizing theoretically the CO_2 injection Enhanced Oil Recovery process. In this type of process, in the reservoir where bitumen or crude oil is present, the pressure is brought up to several MPa, to facilitate the extraction process.

In view of the experimental investigations that will be carried out in this work, many of which take place at room temperature and pressure, it would be interesting to characterize the solubility of CO_2 in bitumen at lower pressures, but none of these sources that specifically analyze the solubility of CO_2 in bitumen studies the system at relatively low pressures or at ambient pressure. Nevertheless, it is conceivable that the CO_2 solubility in bitumen at ambient pressure is much smaller and far from the maximum values observed in these studies, and the results of one of the few studies that analyzed the system at lower pressures, presented in paragraph 2.4, can confirm this hypothesis.

A final important element to be pointed out is linked to the fact that all these sources study the system under thermodynamic equilibrium conditions. In each experiment, the achievement of thermodynamic equilibrium was verified (by monitoring the evolution of the system properties up to their stabilization) before recording the data that were inserted in the graphs shown above. In fact, the experimental results have been compared with theoretical models based on state equations that, by definition, allow the description of a system under thermodynamic equilibrium conditions. Therefore, these sources do not provide information on the CO_2 dissolution in bitumen kinetics. Some interesting results concerning the kinetics of this process and the times associated with it will be presented in paragraphs 2.3 and 2.4.

Table 2.5: Maximum solubility values for different types of bitumen from selected studies.

Type of Bitumen	Max molar fraction, %	Max mass fraction, %	T, °C	P, Mpa	Source
Cold Lake	63	13.43	15	10.95	*Mehrotra and Svrcek [35]*
Athabasca	57	8.93	24	6	*Svrcek and Mehrotra [52]*
Peace River	59	10.72	-3.9	6.1	*Mehrotra and Svrcek [35][20]*
Wabasca	60	12.88	21,9	5.9	*Mehrotra and Svrcek [35]*
Tar Sand Triangle	46	5.08	85	5.52	*Deo, Wang and Hanson [13][27]*
PR Spring	47	6.73	85	5.52	*Deo, Wang and Hanson [13]*

2.3. *CO_2 diffusivity in bitumen*

2.3.1. Overview

Diffusivity can be defined as "*a transport property which is required to calculate the rate of mass transfer of a species due to its molecular diffusion in a medium*" [20].

Equation 2.2, Fick's first law, defines diffusivity D as the proportionality factor that relates the medium-relative mass flux of a species to its spatial concentration gradient opposite to the flux at given pressure and temperature conditions.

$$J = -D\frac{d\varphi}{dx} \tag{2.2}$$

- J is the diffusion flux. It measures the amount of substance that flows through a unit area during a unit time interval.
- D is the diffusion coefficient or diffusivity.
- ϕ (for ideal mixtures) is the concentration.
- x is position.

Since the primary mode of gas dissolution in a bitumen reservoir is through molecular diffusion [11], diffusivity data of gases in bitumen are useful for designing recovery operations based on gas dissolution and several studies have tried to determine diffusivity data, because of this, an accurate value of the diffusion coefficient of CO_2 in bitumen is essential for calculating its dissolution rate [59].

Fick's second law, reported in Equation 2.3, predicts how diffusion causes the concentration to change with respect to time. It is a partial differential equation which in one dimension reads:

$$\frac{\partial\varphi}{\partial t} = D\frac{\partial^2\varphi}{\partial x^2} \tag{2.3}$$

- ϕ is the concentration, a function that depends on location x and time t
- t is time
- D is the diffusion coefficient in dimensions of $length^2\ time^{-1}$
- x is the position

In other words, using models based on the second law of Fick, it is possible to use the diffusivity coefficient D to characterize how the CO_2 concentration profile varies over time.

2.3.2. Experimental procedures

There are various types of experimental techniques to determine the diffusivity of a gas in another fluid. In general, the diffusivity measurement techniques are classified as direct and indirect techniques.

Direct techniques are based on the determination of the composition of the diffusing species along the length of the bitumen sample with time. Direct methods require long time, they are expensive, and the extraction of samples is system-intrusive, making the estimation of dissolved gas in a sample prone to experimental errors.

Indirect techniques consist of the measurement of the physical properties correlated to diffusivity. The indirect measurements can include the measurement of the gas−liquid interface level, the pressure of the diffusing gas, the density of the liquid phase, the refraction of electromagnetic radiation, etc. These techniques measure the changes in property caused by the diffusing species. After the composition of the medium has been determined, a mass-transfer model is then used to calculate the diffusivity. Indirect methods based on properties variations depend on several simplifications, thus producing an error in estimating the effective diffusivity value.

One of the most popular techniques to measure the diffusivity of the gas−liquid systems is the pressure−decay technique, which was introduced by Riazi [43] for reservoir fluids and which is the one used in most of the sources [46][53][56][58][59][63] analyzed for this report. Unlike other conventional techniques, the pressure−decay technique is convenient, simple, and accurate for engineering applications. In the gas and oil industry, this technique is widely used to measure the diffusivity of gases into different products [43].

In this technique the pressure of the gas phase is monitored over time. While the molecules diffuse into the bitumen sample, the cell pressure decreases, until it reaches an equilibrium value corresponding to the thermodynamic equilibrium at those temperature and pressure conditions. At this point, the mass conservation equations on the interface and the diffusion equations in the gas and liquid phases are solved to calculate the numerical value of the diffusivity D.

All works that implement the pressure-decay technique, utilize an experimental setup that generally presents the following components and characteristics:

- A pressure vessel, which holds the CO_2 and the bitumen sample, generally equipped with something to secure the vessel leak-proof.
- A pump, to supply the gas at the desired pressure
- A preheating coil to adjust the gas temperature
- An oven or a water bath, in which the pressure vessel is immerged, connected to a temperature controller system to maintain the wanted temperature during the experiment
- A pressure transmitter to measure the pressure of the system, which is connected to a computer to extrapolate the pressure/time data.

Figure 2.5 shows the schematic diagram of a generic experimental apparatus based on the analysis of the selected studies' experimental setups [46][53][56][58][59][63].

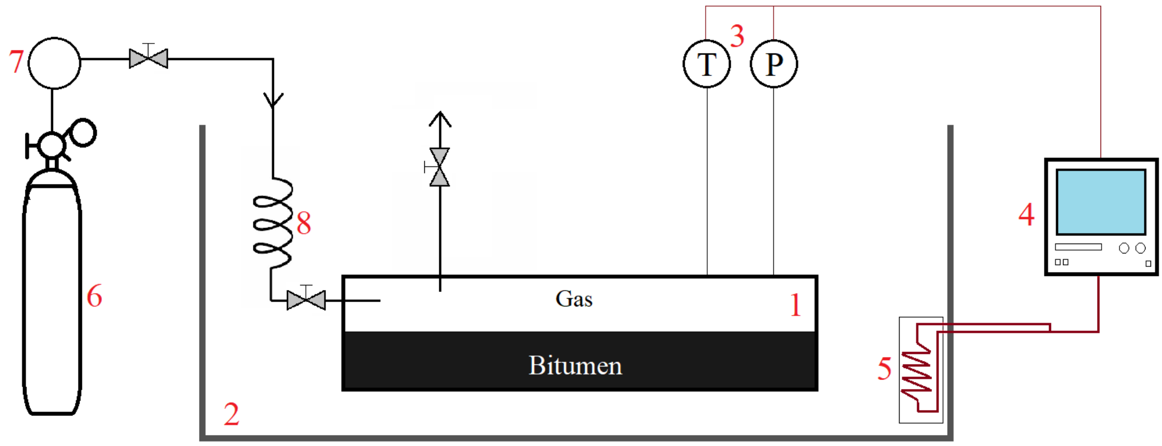


Figure 2.5: Generic schematic apparatus for Pressure-decay experiment to characterize the CO_2 diffusivity in bitumen. 1: Pressure vessel; 2: Oven/water bath; 3: Pressure/temperature transmitters; 4: Computer; 5: Temperature controller; 6: CO_2 bottle; 7: Gas supply system; 8: Pre-heating coil.

2.3.3. Results

In figure 2.6 there is an example of the generic shape of a pressure-decay diagram, based on the results of three different studies [5][57][58]. In this type of diagram, there is the time in hours on the x-axis and the pressure of the system in Mpa on the y-axis. The pressure starts from the system initial value imposed by the pump and decreases progressively until it reaches a plateau that corresponds to the equilibrium pressure and to the achievement of CO_2 saturation in the bitumen sample at those thermodynamic conditions.

In each diagram there can be different curves corresponding to different temperatures (isotherms). On the other hand, in Figure 2.7, there is the general representation of two different curves corresponding to the same temperature value but respectively without and with application of a shear force on the bitumen sample.

By observing the results of the selected studies [5][57][58], it is possible to see how the pressure profile reaches a plateau (equilibrium pressure) after some dozens of hours, suggesting that this is the order of magnitude of the time necessary to achieve equilibrium in these thermodynamic conditions (pressure between 2 and 8 Mpa) and thus giving an idea of the process kinetics.

Moreover, figure 2.7 shows that mixing the bitumen sample, and more generally the application of a shear force, facilitates the dissolution of CO_2 and the achievement of equilibrium. It is evident that when a shear effort is applied, there is a sudden drop in the system pressure and therefore an increase of the absorbed CO_2 in the sample: the increase in shear force increases the speed of the absorption process.

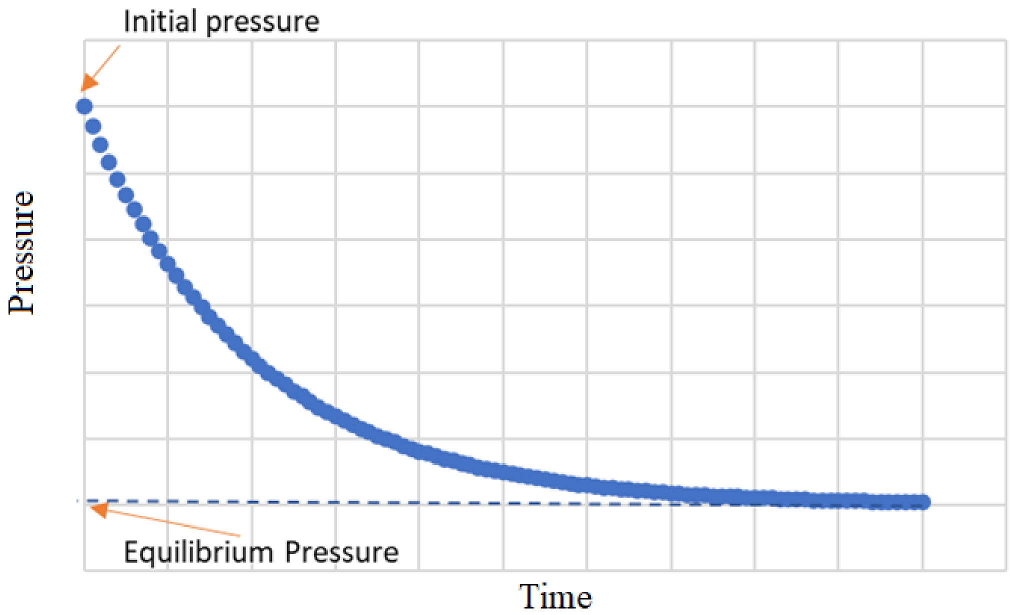


Figure 2.6: Example of a generic pressure-decay curve shape: the pressure in the cell decreases progressively until it reaches a plateau corresponding to the equilibrium pressure.

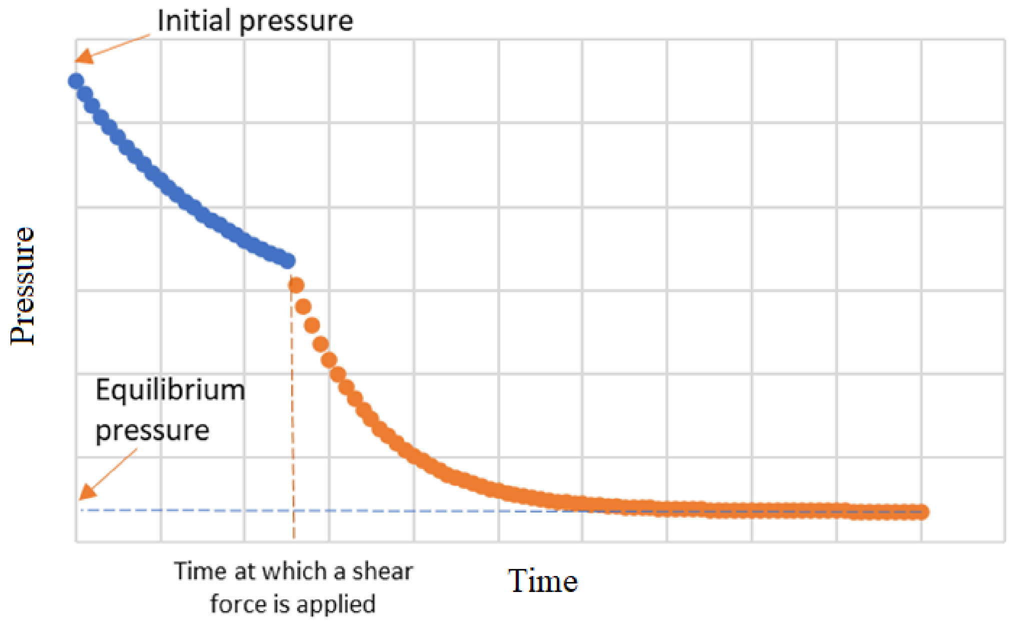


Figure 2.7: Example of a generic pressure-decay curve shape: when a shear force (mixing) is applied, the pressure evolution starts to decrease faster, and it reaches a new equilibrium value.

Table 2.6 gives the initial and equilibrium pressure values for an experiment conducted at 30 °C, 50 °C and 70 °C from Behzadfar [5].

Table 2.6: Parameters from the Analysis of the Pressure-Decay Experiments, modified from Behzadfar [5].

Temperature, °C	Initial pressure, bar	Equilibrium pressure, bar
30	24.23	*22.51*
	40.34	*35.66*
50	23.11	*21.22*
	50.08	*37.96*
70	22.44	*11.15*
	47.94	*45.06*

Figure 2.8 shows an example of the generic trend of a curve that describes evolution of the CO_2 mass diffused in bitumen over time (based on the results of some of the selected studies [5][57]), directly related to the pressure/time diagrams previously showed. These diagrams have the same shape as the previous ones, with the achievement of a plateau that corresponds to a thermodynamic equilibrium condition. The values shown on these diagrams are generally CO_2 absolute mass values or CO_2 mass or mole fraction values.

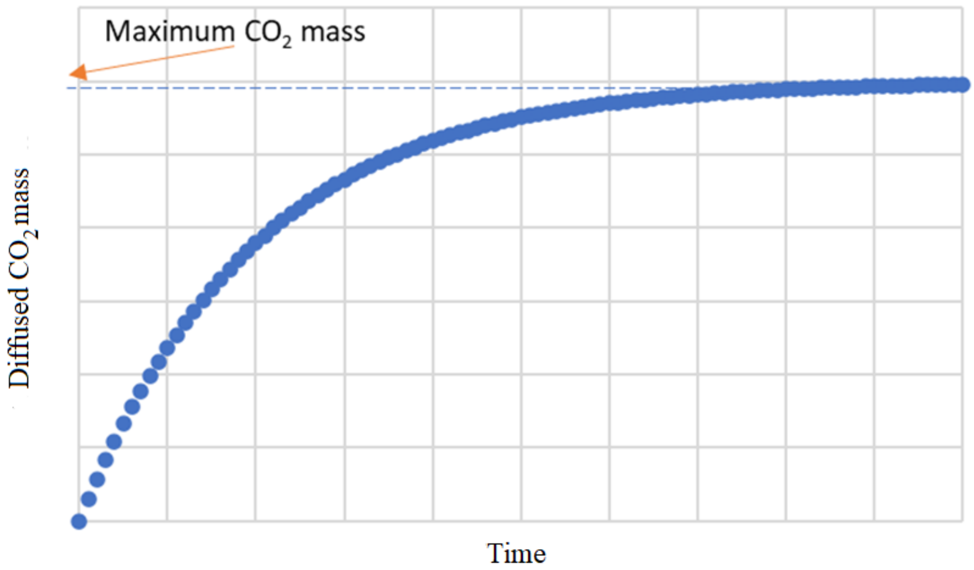


Figure 2.8: Generic shape of a diffused CO_2 mass vs time curve.

Table 2.7 shows the CO_2 saturation solubility values for two different bitumen samples (Athabasca Syncrude and Suncor Coker Feed, from Upreti [57]). Figure 2.9 directly compare these solubility values with the values of Haddadnia et Al. [17], which refer to an Athabasca bitumen sample too. It can be said that the solubility data of the two studies coincide when the investigated temperature is similar.

The solubility data reported in table 2.7 can be compared with the solubility results of Haddadnia et Al. [17]. As already stated, there is a relatively good experimental agreement between the results of two studies: solubility values expressed in mass fraction are close when referred to comparable temperatures, any inconsistence is due to unforeseeable differences in the composition of the three samples.

Table 2.7: CO_2 saturation mass solubility values for two different Athabasca bitumen samples, modified from Upreti [57].

Type of Bitumen	Pressure, bar	Temperature, °C	Saturation mass fraction, %
SCF (Suncor Coker Feed)	40	25	*6.36*
		50	*5.15*
		75	*4.28*
		90	*3.97*
	80	50	*9.09*
		90	*5.74*
SYN (Syncrude)	40	25	*5.96*
		50	*4.74*
		75	*4.32*
		90	*3.59*
	80	50	*8.66*
		75	*6.88*
		90	*5.74*

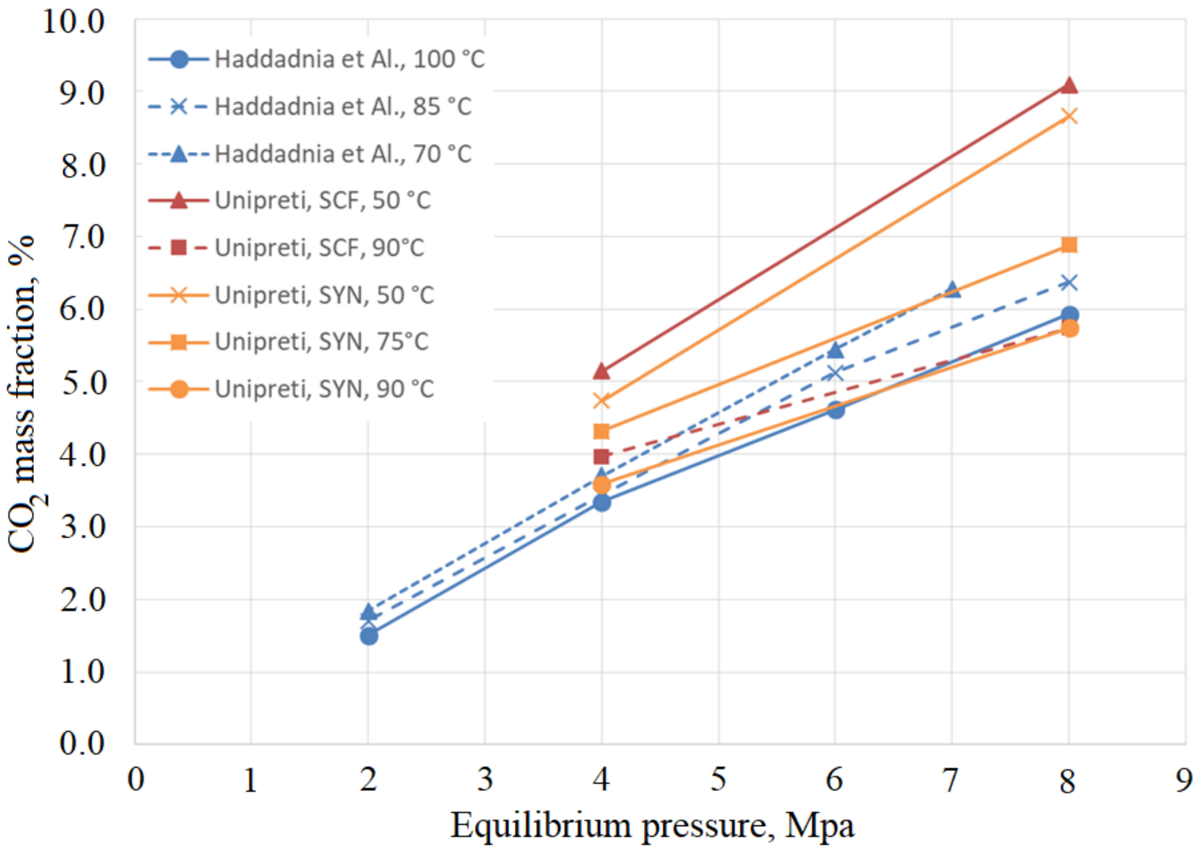


Figure 2.9: Comparison of solubility data obtained in Haddadnia et Al. [17] (in blue) and in Unipreti [57], for two type of Athabasca bitumen samples (in red and yellow).

Behzadfar et Al. [5] have analyzed how CO_2 diffusivity in bitumen varies as a function of CO_2 mass fraction in the sample. The diffusivity/CO_2 mass fraction curves present a maximum value: as the CO_2 amount in the system increases, the diffusivity of the latter first increases and then decreases to reach a constant saturation value. This behavior can be explained by considering that, as already explained, by increasing the dissolved CO_2 amount in bitumen, its viscosity decreases, facilitating the molecular diffusion of the gas, but when a certain concentration is reached, the CO_2 molecules concentration hampers further diffusion, in other words, after a certain concentration, the CO_2 molecules themselves prevent the diffusion of a greater quantity of gas and therefore a constant saturation value is reached [5].

Table 2.8 shows some diffusivity values expressed in m^2/s, for two different samples of Athabasca bitumen as a function of temperature and pressure [57], and figure 2.10 reports these results on diffusivity/temperature plot and compares them with the diffusivity results of Upreti and Mehrotra [58] (at 5 Mpa).

Figure 2.10 show that CO_2 diffusivity increases with temperature. This behavior may be attributed to the increased kinetic energy of the gas and bitumen molecules accompanied by reduction in bitumen viscosity that facilitates mass transfer [5][57][59].

Table 2.8: Diffusivity values for SCF and SYN Athabasca bitumen, modified from Upreti [57].

Type of Bitumen	Pressure, bar	Temperature, °C	Diffusivity (m^2/s)
SCF (Suncor Coker Feed)	40	25	*1.9E^{-10}*
		50	*2.41E^{-10}*
		75	*3.83E^{-10}*
		90	*4.33E^{-10}*
	80	50	*5.92E^{-10}*
		90	*1.02E^{-09}*
SYN (Syncrude)	40	25	*1.34E^{-10}*
		50	*2.37E^{-10}*
		75	*3.74E^{-10}*
		90	*4.28E^{-10}*
	80	50	*3.98E^{-10}*
		75	*7.49E^{-10}*
		90	*9.32E^{-10}*

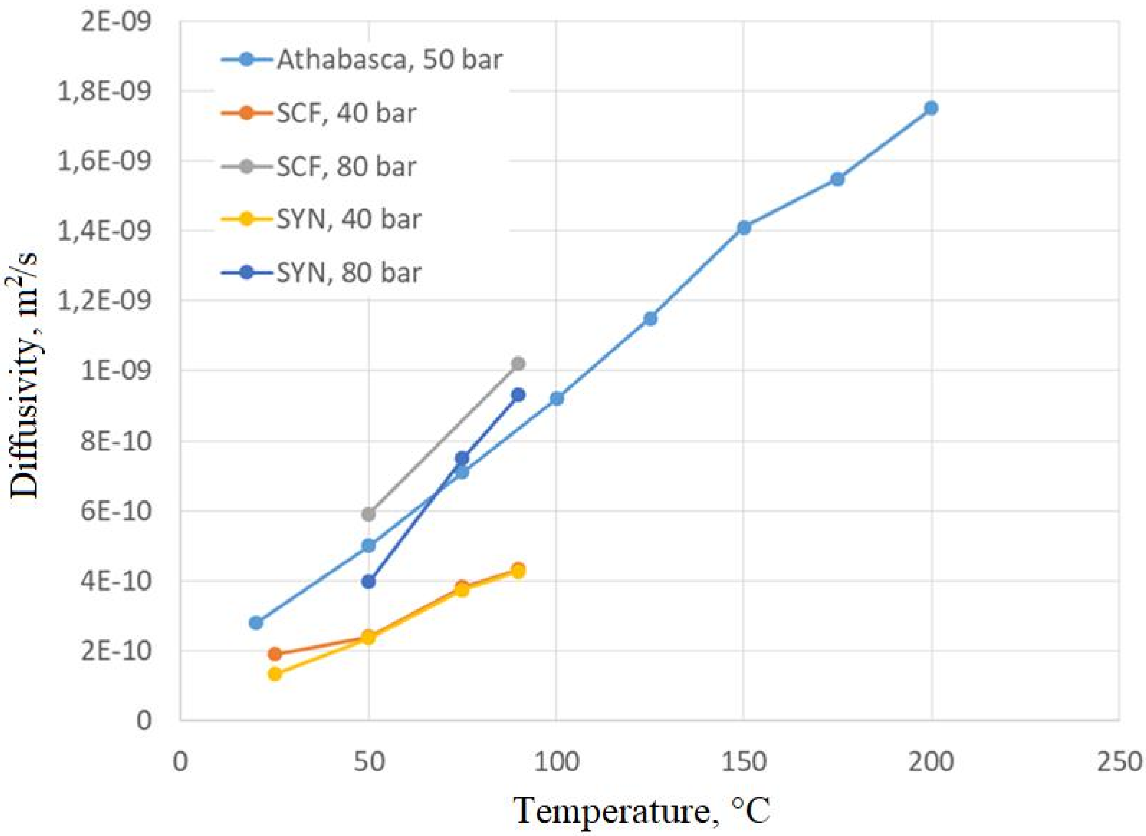


Figure 2.10: Comparison between the diffusivity data of two different studies at 40, 50 and 80 bar, from Upreti and Mehrotra [58][57].

It is important to notice that also for these studies analyzed in this section of the report, the bitumen-CO_2 system is investigated at relatively high pressures (dozens of bars, > 20 bars).

In this section, however, some data that can be associated with the evolution over time of the properties of the system during the process of absorption or dissolution have been analyzed, in other words, the kinetic aspect of this process has been partially characterized, at least qualitatively, allowing to have an idea of the order of magnitude of the time needed to achieve equilibrium and saturation in these thermodynamic conditions. This is a type of information particularly interesting in relation to this work. Nevertheless, it would be much more interesting to obtain this information in relation to a thermodynamic system at much lower pressures, as well as to characterize this evolution quantitatively with a kinetic model.

In addition, all these studies analyze the process of CO_2 absorption or dissolution in bitumen, but no study presented until this point has investigated the thermodynamics or kinetics of the spontaneous desorption process, which is central to this work. All these elements are partially analyzed in the study that will be presented in section 2.4.

In general, there is very little information in the literature about the kinetics of the process of CO_2 dissolution in bitumen and even less information about the process of spontaneous desorption. This is because the system is currently interesting only in relation to the practical application associated with CO_2 injection EOR, which is carried out at high pressures, and which is interesting only in terms of equilibrium thermodynamic characterization and for which no data associated with the kinetics of the process seems to be the subject of interest in the studies analyzed.

2.4. *Kinetics of CO_2 diffusion in bitumen and CO_2-bitumen mixtures storage stability*

2.4.1. Overview

Apeagyei et Al. [2] analyze the CO_2-bitumen system at room temperature and relatively low pressure (40 psi = 2.76 bar), trying to characterize and model the CO_2 solubilization kinetics as well as the CO_2 release kinetics when the bitumen is exposed to free air conditions.

This study focuses on another type of application other than that investigated by the works seen so far. In fact, if the works previously analyzed study the thermodynamic CO_2-bitumen system in relation to the CO_2 injection process (EOR), in this case the system is analyzed in relation to the production of bituminous mixtures for pavement construction, such as hot mix asphalt (HMA), warm mix asphalt (WMA) and cold mix asphalt (CMA). These mixtures are produced by coating mineral aggregates with low-viscosity bitumen.

For this process, the reduction of bitumen viscosity is quite important: at ordinary temperatures, paving grade bitumen is a highly viscous material with viscosity on the order of 100-1000 Pa·s at 60 °C, and substantial efforts are necessary to reduce bitumen viscosity, in the form of energy application, additives or solvents. It is in fact necessary to achieve the right mixing viscosities to produce the asphalt mixture.

Today, most methods to reduce bitumen viscosity consist of using energy to heat the bitumen (up to 160°C). This method, which is not sustainable, releases important amounts of greenhouse gases. Other viscosity-reducing technologies (foaming with water, waxes, emulsification) allow to partially decrease viscosity so that the process can be carried out at 150 °C. Another solution consists of the utilization of organic solvents (kerosene, naphthalene, white spirit, gasoline), but these substances are not environmentally sustainable.

Apeagyei et Al. [2] propose to exploit the CO_2 near its critical conditions to act as an effective viscosity-reducing solvent in paving grade bitumen. This solution would allow to reduce bitumen viscosity for applications at lower temperatures, reducing the paving industry CO_2 emission footprint.

Two grades of bitumen with different viscosities have been used in this study. This work aimed to evaluate the kinetics of CO_2 diffusion in bitumen using gravimetric techniques at multiple pressures and temperatures and to characterize the CO_2 release kinetics of carbonated bitumen after free air exposition, to evaluate its CO_2 stockage stability.

The results were used to determine if CO_2 could be used as a solvent for producing a more sustainable bitumen for paving application. An important feature of this study, which makes it quite interesting for the purpose of this work, is the fact that compared to previous studies, it uses CO_2 at subcritical conditions (20-25°C and pressures 0.3 – 2 MPa), conditions not too far from the ambient conditions that will constitute the first step of this work.

2.4.2. Materials, models, and methods

Two different bituminous binders, one 50 Pen and one 190 Pen were used to produce the CO_2-modified bitumen. The two binders present some differences in terms of properties.

A scheme of the experimental setup utilized in this work is presented in Figure 2.11. This setup is quite simple: it consists of a compressed CO_2 gas cylinder connected to a Parr high-capacity pressure vessel that can be subjected to pressures up to 20 bars and temperatures up to 80 °C. The pressure vessel is equipped with a sample holder. The bitumen samples were placed in the vessel. Carbon dioxide at 40 psi and 300 psi (2.76 bar and 20.7 bar), and at temperatures close to the critical temperature of CO_2 (22-25 °C) was employed for the experience. Both the experimental setup and the sample characteristics present some similarities with the ones of this work, thus making the results of this study quite significant.

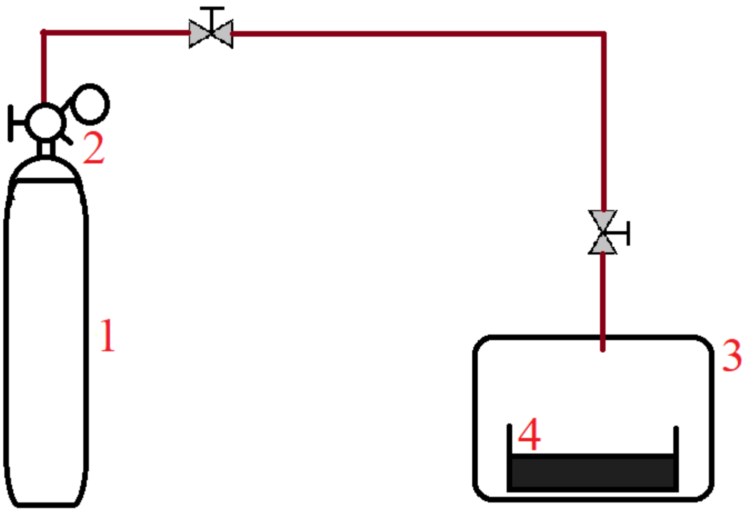


Figure 2.11: Schematic of the CO_2 system used for modifying bitumen, modified from Apeagyei et Al. [2], 1: CO2 bottle; 2: Pressure gauge; 3: Sample vessel; 4: Bitumen sample.

The CO_2 uptake experimental points have been used to develop a simple model. The CO_2 uptake can be defined as "*the ratio of the amount of CO_2 absorbed at a given time to the initial dry mass of the sample at the beginning of the test*", as indicated by equation 2.4.

$$Mass\ uptake = M_t = \frac{w_t - w_0}{w_0} \quad (2.4)$$

Where w_0 is the initial dry mass of the given material and w_t is the mass after time t.

The following model (Peleg, 1988) [42], expressed by equation 2.5 and equation 2.6, has been used in this work:

$$M_t = \frac{t}{C_1 + t \cdot C_2} \quad (2.5)$$

$$C_1 = \frac{1}{k x_e^2}; \qquad C_2 = \frac{1}{x_e} \quad (2.6)$$

The model parameter C_1 represents the CO_2 diffusion rate, while C_2 is a measure of the equilibrium CO_2 value (it is the reciprocal of the maximum CO_2 uptake). k is the diffusion process kinetic rate and x_e is the maximum CO_2 uptake.

2.4.3. Kinetics of CO_2 diffusion in bitumen: results

Kinetics of CO_2 diffusion in bitumen at 20°C were determined by placing the bitumen sample in a pressure vessel up to 170 hours and monitoring the mass variation by using an ultra-sensitive weighing balance (resolution 0.1µg).

Figure 2.12 shows the kinetics of CO_2 diffusion for the two bitumen samples plotted as a function CO_2 mass uptake vs time. The error bars shown in Figure 2.12 represent the standard deviation of the mean CO_2 uptake experimental points.

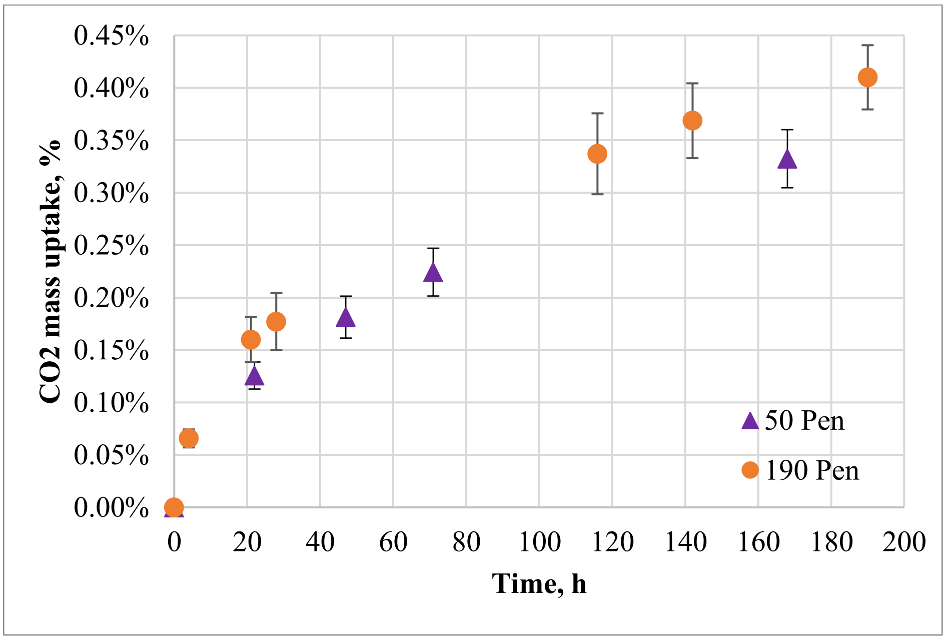


Figure 2.12: CO_2 diffusion kinetics in bitumen at 20°C and 40 psi, modified from Apeagyei et Al. [2].

The equilibrium uptake values for the two binders are 0.41 ± 0.0306 wt % and 0.3324 ± 0.0277 wt % for 160 pen and 50 pen, respectively.

The equilibrium CO_2 uptake obtained in this study is comparatively lower than reported values of CO_2 diffusion in bitumen that have been reported by previous studies. This could be attributed to the fact that majority of the reported CO_2 diffusion studies were conducted at or near supercritical conditions (relatively high pressures).

The changes in CO_2 concentration in bitumen over time were predicted using Eq. 6 (Peleg model). A least square regression analysis was used to estimate the model parameters C_1 and C_2. The experimental points together with the Model curves are shown in Figure 2.13.

The C_1 data suggest that the rate of CO_2 uptake is relatively higher in 50 Pen compared with 190 Pen bitumen. The C_2 value suggest that the theoretical equilibrium CO_2 uptake under the experimental conditions of 20°C and pressure of 40 psi in 160 Pen is comparable to that in 50 Pen bitumen.

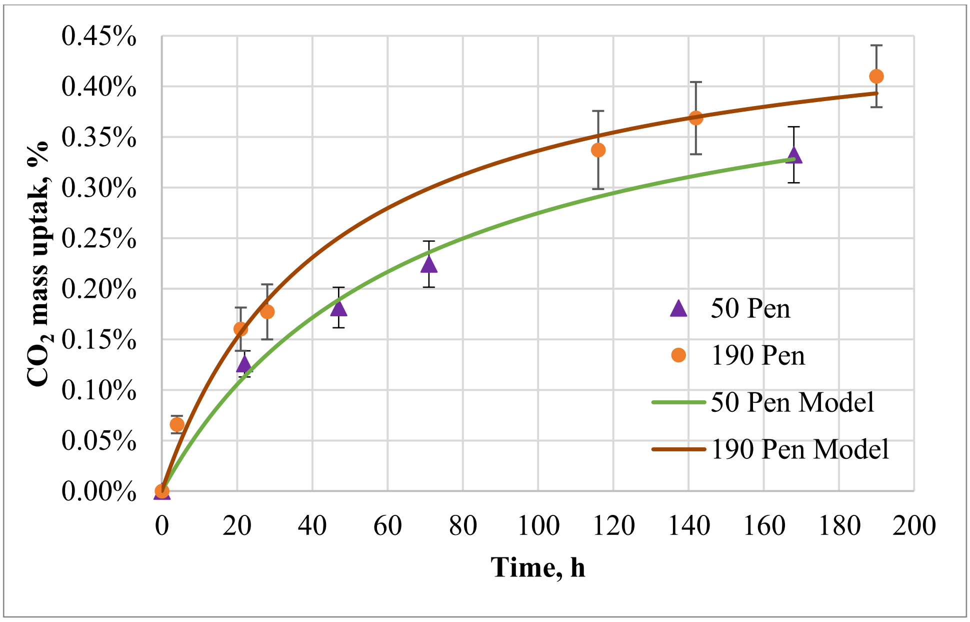


Figure 2.13: Peleg model fit to CO_2 uptake by bitumen at 20°C and 40 psi, modified from Apeagyei et Al. [2].

2.4.4. Storage stability of CO_2-bitumen mixtures: results

The stability of the carbonated bitumen has been characterized by comparing the kinetics of pressurized CO_2 diffusion in bitumen with CO_2 release from bitumen after free air exposition (1 atmosphere, 20 °C).

Figure 2.14 shows the CO_2 release rates of carbonated bitumen after free air exposition. Bitumen samples were previously exposed to CO_2 at 40 psi for up to 200 hours. The rate of CO_2 release from bitumen was higher than the CO_2 diffusion rate, which could be attributed to the fact that diffusion occurred under higher pressure conditions.

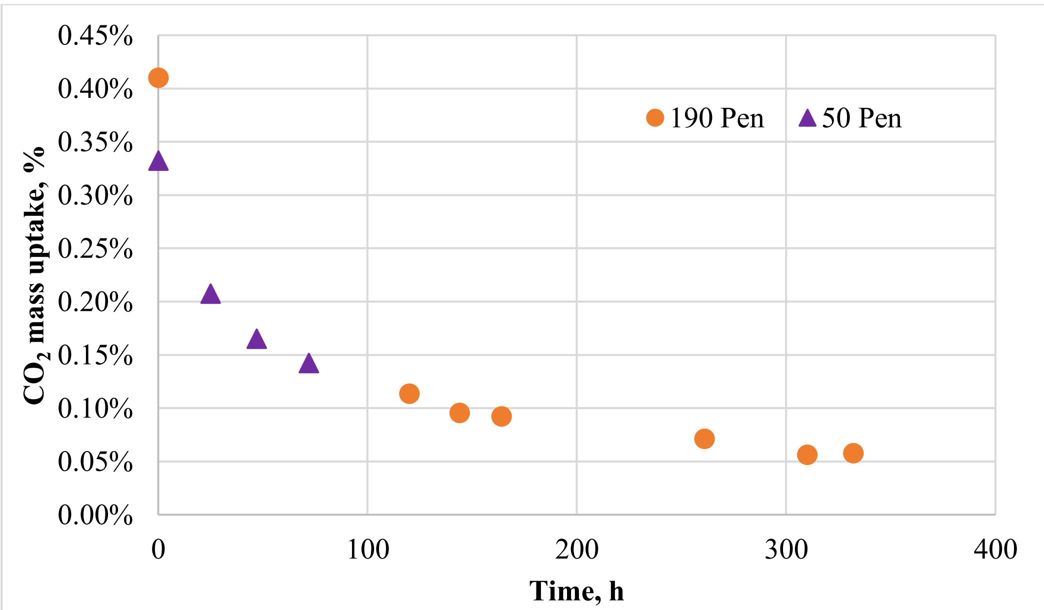


Figure 2.14: CO_2 release rates of from modified bitumen under ambient conditions. Bitumen samples were previously conditioned in CO_2 at 40 psi for up to 200 hours, modified from Apeagyei et Al. [2].

Another important observation that could be made from the curve trend in Figure 2.14 is that the time scale required for CO_2 release from bitumen is on the order of some days. This imply that carbonated bitumen appears to be relatively stable under ambient condition for far greater times compared to typical mixing times for bituminous mixtures. In fact, even after almost 200 hours exposition to free air conditions, the bitumen retained a CO_2 mass fraction of about 0.065 ± 0.009%, which is comparable to CO_2 concentration of approximately 0.063% in air [16].

2.5. Characterization of the CO_2-bitumen interactions

In Li et Al. study [29] the molecular dynamics method has been used to simulate the association systems of resin, resin-asphaltene and asphaltene (which generally constitute a significant fraction of bitumen). The density distributions and adsorption capacities of CO_2 in these association systems have been characterized and the interaction energies in the three systems were determined.

Based on classical Newtonian mechanics, molecular dynamics is a computer simulation method that can analyze intermolecular forces and their variations. It has been used in this study to characterize the adsorption and dissolution of CO_2 in resin and asphaltene at the molecular level.

Because of the complex chemical composition of asphaltene and resin, it is difficult to establish a specific chemical structure for their characterization. Therefore, based on the structural parameters of different resins and asphaltenes, other studies have established a series of molecular models of resins and asphaltenes [7][28], which have been used in Li et Al. study.

The amount of CO_2 adsorbed by different association systems increases as pressure increases. The resin association system has the highest CO_2 capacity, followed by the resin-asphaltene association system, and finally by the asphaltene association system.

To clarify the interaction between CO_2 and the association system, the interaction energy (E_{Inter}) between CO_2 and resin, CO_2 and resin-asphaltene, and CO_2 and asphaltene has been calculated. Intermolecular interaction reflects the strength of the bond between CO_2 and the association system. The expression to calculate E_{inter} is expressed in equation 2.7.

$$E_{inter} = E_{Total} - (E_{oil} + E_{CO_2}) \tag{2.7}$$

Where, E_{Inter} is the interaction energy between gas molecule and the association system, kcal/mol; E_{Total} is the total energy of gas molecule and the association system, kcal/mol; E_{Oil} is the energy of the association system, kcal/mol; and E_{CO2} is the energy of CO_2, kcal/mol.

Table 2.9 compares the interaction energy between CO_2 and the three association systems at 298 K and 0.5 MPa. The strength of CO_2 interaction with resin, resin-asphaltene and asphaltene respectively decreases.

Table 2.9: Interaction energy between CO_2 and ass. system at 298 K and 0.5 MPa, modified from Li et Al. [29].

Association System		**E_{total}, kcal/mol**	**E_{oil}, kcal/mol**	**E_{CO2}, kcal/mol**	**E_{inter}, kcal/mol**
CO_2	Resin	410.13	487.72	60.67	***-138.26***
	Resin-Asphaltene	3090.38	3155.31	51.49	***-116.42***
	Asphaltene	6015.57	6043.07	29.63	***-57.13***

The energy of interaction of a generic physical adsorption is around 10 – 40 kJ/mol (2.5 – 9.5 kcal/mol) and the adsorption heat of a generic chemical adsorption is around 20 – 400 kJ/mol (5 – 95 kcal/mol) [4]. The results on the interaction energies provided by this study and presented in Table 11 allow to conclude that the interaction between the CO_2 molecules and the materials in question is an interaction that involves the formation of chemical bonds and not weaker interactions of physical nature as the Wan der Walls forces.

2.6. Thermal and chemical treatments on asphalt

Jalilov et Al. [24], reports an improved method for activating asphalt to produce ultra-high surface area porous carbons.

The chemical-physical treatment of asphalt to obtain a high surface area material with excellent CO_2 capture properties has been the subject of numerous studies. Nevertheless, when asphalt is subjected to such treatments, it undergoes substantial structural changes, leading to the formation of porous materials with properties far enough from the materials that will be studied in this work (bitumen). In any case, the results of this study are reported in this paragraph because, although the results are substantially different, from a conceptual point of view one of these bitumen formulations has been subjected to a treatment to modify its reactivity with CO_2. (A chemical treatment instead of a thermal treatment).

In Jalilov et Al. study [24] Pretreatment of asphalt (untreated Gilsonite, uGil) at 400 °C is used to remove the more volatile organic compounds to form a pretreated asphalt material with a larger fraction of higher molecular weight π-conjugated asphaltenes. Then, an activation at 900 °C gives an ultra-high surface area porous carbon material (uGil-900) with a mixed micro and mesoporous structure. uGil-900 shows enhanced room temperature CO_2 uptake capacity at 54 bar of 154 wt% (35 mmol g^{-1}).

The uGil-900 is produced directly from an inexpensive asphalt carbon source, and because of this it appears to be quite interesting. These observations indicate that the porous materials from asphalt are promising inexpensive sorbents for industrial applications where CO_2 needs to be removed from natural gas streams and that, more generally, a treated material obtained from a bitumen sample can be effectively used to sequestrate and stock CO_2.

2.7. Gas Chromatography of bitumen fumes

Part of this study (the third step) is to characterize the volatile components released when the bituminous materials under study are heated to relatively high temperatures (80°C - 160°C), corresponding to the temperatures to which such materials are generally subjected during their fabrication or their application.

It is important to carry out a comprehensive characterization of the components released according to the temperature applied, for various reasons:

- As mentioned above, these materials are often subject to temperatures above 80°C, for example during the manufacture of road paving, where bitumen is heated to reduce its viscosity and allow it to be mixed with inert materials.
- Bitumen fumes generated by the heating of bituminous materials contain substances which have been confirmed to be toxic, irritant, and carcinogenic when inhaled, therefore a characterization of these volatile components is necessary to define the exposure risk.

- The subject of the study is the solubilization of CO_2 in bitumen, it is important to remember that the temperature increase implies the solubilization of lower amounts of CO_2 at the same saturation pressure, therefore it is interesting to understand how the temperature increase affects the stored CO_2 in the bitumen samples under study, whether it involves a release of the latter and whether such release is substantial or negligible: in this way it is possible to characterize the temperature range in which bitumen is actually usable as a CO_2 storage material.

One of the most common analytical techniques to characterize the release of volatile components following an increase in temperature, is Gas Phase Chromatography (GPC). Gas Phase chromatography is the process of separating compounds in a mixture by injecting a gaseous sample into a mobile phase, the carrier gas, which is passed through a stationary phase. The mobile phase is an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of viscous liquid on an inert solid support inside a glass or metal tubing called a column. The column through which the gas phase passes is inserted in an oven where the gas temperature is controlled, and in such a way the eluent coming off the column is monitored by an electronic detector [18][19].

It is necessary to distinguish two types of gas chromatography:

- The GPC-FID (Gas Phase Chromatography – Flame Ionization Detector) is a Gas Chromatography that uses the FID technique to characterize the analytes in the gas stream. The FID is based on the detection of ions formed during the organic compounds' combustion in a hydrogen flame.
- The GPC-MS is an analytical method that combines gas-chromatography and mass spectrometry, which is an analytical technique that is used to measure the mass-to-charge ratio of ions. This technology allows a better substance identification than GPC-FID. It is not possible to make an identification of a specific molecule by Gas chromatography using a Flame ionization detector, because this technique cannot distinguish multiple molecules that take the same amount of time to travel through the column.

Although the characterization of bitumen fumes is particularly interesting for the reasons listed above, it has not been possible to find much information in the scientific literature about the results of the GPC technique applied to this material.

Sutter et Al. [51][63] describe the principle, the domain of application and method used in the gas phase chromatography experimental technique for the characterization of components within a sample of bitumen fumes. The work illustrated in the report carried out the experimental analysis using an *AGILENT model 5973 chromatograph* and a *ZEBRON ZB-5HT INFERNO 30 m x 0,32 mm x 0,25 μm column*. The chromatograph temperature program conditions are:

- Constant temperature of 45°C for 7.5 min
- Temperature gradient at 100°C/min up to 260°C
- Constant temperature of 260°C up to 20 min of analysis

To better characterize the nature of the volatiles components that are released when the bitumen is heated, the temperature program described above has been applied on two different samples of alkane mixtures: a C_8-C_{20} sample and an even-C_{10}-C_{40} sample. In this way it was possible to obtain the chromatogram associated with the C_8-C_{40} alkanes and then identify the peaks associated with each alkane, to compare them with the bitumen fumes chromatogram, to understand the nature of the components released. Figures 2.15 and 2.16 show the chromatograms of the C_8-C_{20} solution and of the even-C_{10}-C_{40} solution, together with the temperature program chosen for the method.

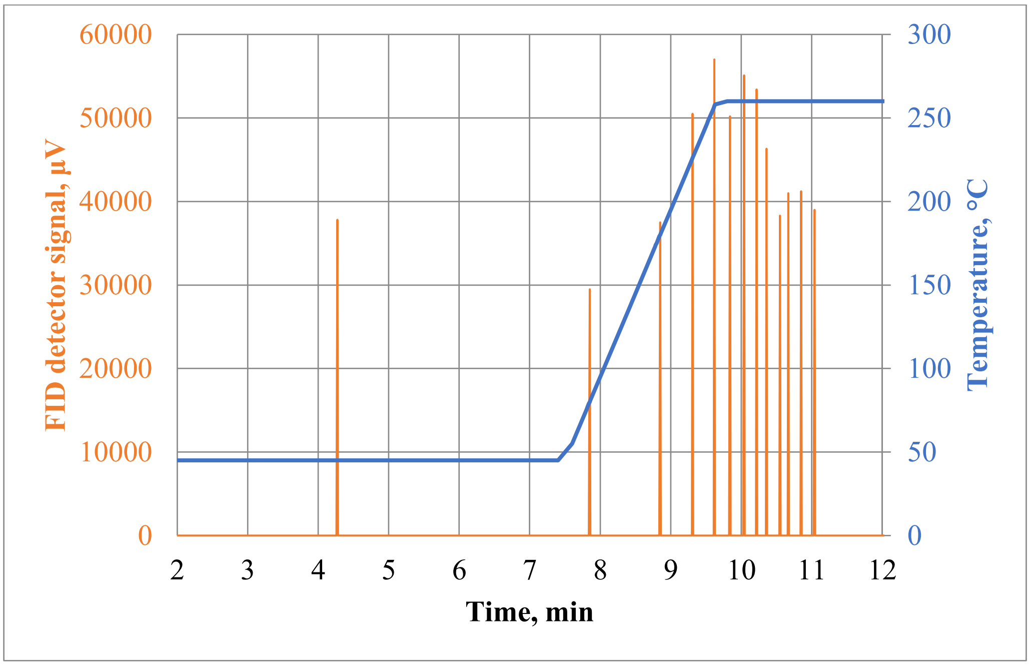


Figure 2.15: Chromatogram of the C_8-C_{20} mix, modified from Sutter et Al. [51].

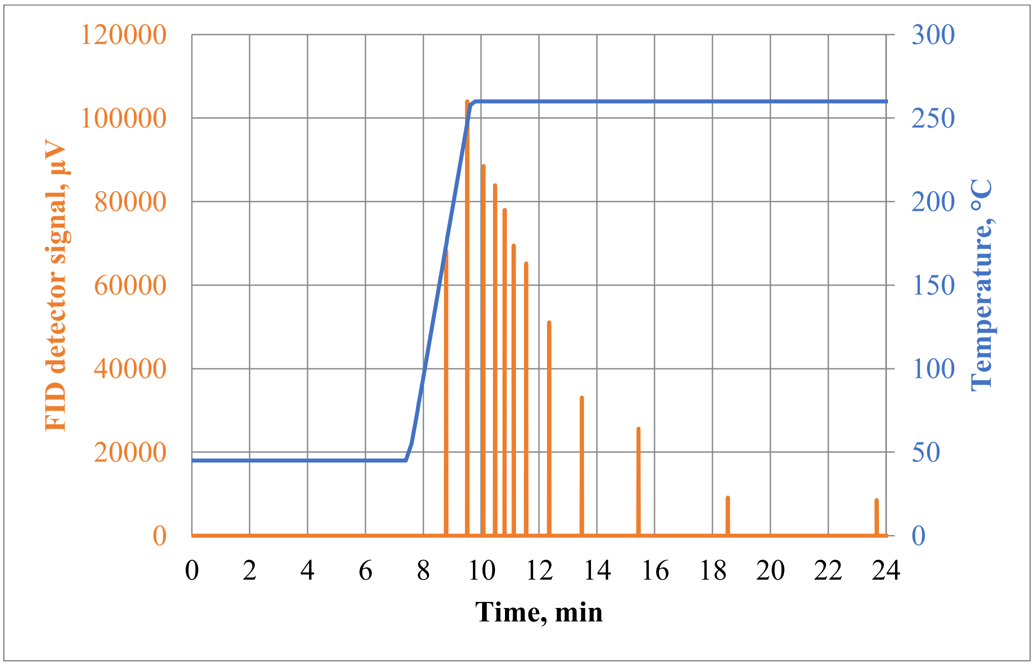


Figure 2.16: Chromatogram of the even-C_{10}-C_{40} mix, modified from Sutter et Al. [51].

The results of Sutter et Al. [51] show that the compounds from the bitumen fumes form a cluster between 9 and 13 minutes, indicating the presence of C_{12}-C_{24} alkanes. On the other hand, the analysis of the construction site's sample shows a chromatogram slightly offset over time with respect to the condensate chromatogram, due to the high variability of compositions of the bitumen used and how it is applied in materials formulations.

2.8. Conclusions

This chapter is the result of a bibliographic research work that revolves around the gaseous carbon dioxide dissolution process in materials such as bitumen and RAP (Reclaimed Asphalt Materials).

After a general chemical-physical characterization of the materials in question, the economic, practical, and applicative interest of the CO_2-bitumen thermodynamic system has been described. Many studies have in fact analyzed the characteristics of this system in relation to what is now the most common practical application: the CO_2 injection process in the Enhanced Oil Recovery technologies domain, a type of technological process particularly exploited in North America.

The main interest of the works that study the system in relation to this process is that of characterizing some properties of the bitumen-CO_2 mixture, in particular CO_2 solubility and bitumen viscosity. The solubilization of CO_2 in bitumen leads to a significant decrease in its viscosity, facilitating its extraction and reducing the associated costs. A thorough analysis of this work has allowed to characterize the solubility of various types of bitumen at different temperatures and pressures.

This solubility, which increases with increasing pressure and decreases with increasing temperature, can reach up to 60 mol% (about 12 wt%). Nevertheless, although the solubility value is very high and promising, all studies analyzed study the system at relatively high-pressure conditions (dozens of bars). The solubility of CO_2 in bitumen at lower pressure conditions and close to ambient pressure has been characterized by very few studies, which have reported much lower values.

The results of another group of studies related to the CO_2-bitumen system, but focused on the characterization of CO_2 diffusivity, allowed to appreciate the phenomenon of CO_2 solubilization in bitumen from a "kinetic" point of view, in terms of *variation over time* until the thermodynamic equilibrium is reached. These results are reported in the form of pressure-decay plots over time or amount of CO_2 absorbed over time. Nevertheless, even in this case the pressures investigated are very high (> 20 bars), and therefore the results are interesting, but they fail once again to provide a complete characterization of the system at conditions closer to ambient ones.

Apeagyei et Al. study [2] is one of the few to analyze the system under conditions close to those of the environment (and the only one that provides interesting results, although limited). This study investigates the CO_2 diffusion in bitumen kinetics at 20 °C and 2.75 bar, showing that in about 150-180 hours two different bitumen samples absorb up to 0.41 wt% and 0.33 wt% of CO_2 respectively, confirming a much lower solubility under low pressure conditions.

This study also provides information on the storage stability of the CO_2-bitumen mixture: the stability of the CO_2-bitumen mixtures (carbonated bitumen) was evaluated by comparing the kinetics of pressurized CO_2 diffusion in bitumen with CO_2 desorption from bitumen under ambient conditions (20°C and 1 atmosphere). This information was deemed important to establish because there has been very little published data on the kinetics of CO_2 absorption and desorption (degassing) from bitumen. Among the most interesting results there is the fact that the time scale required for CO_2 desorption from bitumen is on the order of days, and that even after almost 200 hours storage under ambient conditions, the carbonated bitumen retained residual CO_2 concentration of about 0.065 ± 0.009%, which was more than twice the CO_2 concentration of approximately 0.027-0.037% in air.

Some other studies have tried to characterize the nature of the interactions responsible for the solubilization of CO_2 in bitumen, by means of a molecular dynamic method used to construct the association systems of resin, resin-asphaltene and asphaltene. The interaction energy obtained from the simulation suggests an interaction associated with the presence of chemical bonds.

Further studies have finally proposed some chemical-physical asphalt treatment processes to produce materials with high CO_2 capture capacity.

Sutter et Al. [51] do a characterization of the bitumen fumes composition by using a GPC technique, by comparing the results with a reference obtained by using alkanes mix, to identify which alkanes are released when the bitumen samples are heated. The experimental method and temperature program used in this report has been used to define the last step of this work.

3. Experimental setup, materials, and methods

3.1. *Materials*

The samples utilized in this work consist of three different types of materials, which have been supplied by *TOTAL's research center (CRES)* based in Solaize (Lyon, Auvergne-Rhone-Alpes, France). The materials have been selected by the research center with the aim of characterizing their CO_2 solubilization and retention capacities and assessing the technical and economic interest of this process, by defining the optimal physical conditions for its realization and, possibly, industrial implementation.

The materials in question are two types of bitumen: a classic bitumen formulation, and modified bitumen formulation (with the addition of some additives), and one type of asphalt pavement aggregate.

The presence of the additives in the formulation could be associated to a greater capacity of the material to absorb and retain CO_2: the main purpose of this work is to verify the existence and extent of this phenomenon, to verify the existence of substantial differences in terms of maximum capacity and kinetics between the two formulations.

The other investigated material is an asphalt mix (or asphalt pavement aggregate or asphalt concrete), which is a mixture of gravel, sand, and a hydrocarbon binder, such as bitumen. The supplied material has variable grain size, starting from very small granules that constitute a fine powder, up to large pieces with a characteristic size of the order of 2-3 cm. Figure 3.1 shows the supplied samples of the three materials used in this work.

Figure 3.1: Samples of the selected materials.

3.2. Experimental setup and methods

3.2.1. Samples preparation

The samples realized for this work experience have been prepared following a precise procedure which will be briefly explained in this paragraph.

The granular material that constitutes the bituminous aggregate has been sieved several times to select the material with a grain size between 1 mm and 2 mm.

The bituminous aggregate samples consist of a heat-resistant glass dish/plate with a diameter of 8.5 cm, in which a certain amount of aggregate is placed (about 50 g).

The bitumen samples are in the form of thin layers. The two bitumen formulations provided have a particularly high viscosity at room temperature, thus excluding the possibility of producing a thin layer without prior heating. For the preparation of each sample a certain amount of bitumen is placed within the heat-resistant glass dish/plate, which is then heated in an oven at 160 °C. Due to the heating the bitumen is then arranged in the form of a thin layer. As a precautionary measure, the plates in which the samples are placed to be heated are covered with a glass cover, to limit as much as possible, the contact with the atmosphere inside the oven and thus avoid any oxidation process. After the heating process, the samples are left to cool and stabilize for a whole day before being used for experiences.

The containers used have a diameter of 8.5 cm, with the aim of obtaining bitumen layers with the same thickness as those used in CRES experiments, the amount of bitumen placed in each dish is about 15 grams. In this way the samples are about 4 mm thick. An example of such samples is shown in figure 3.2.

Figure 3.2: Bitumen and RAP samples in 8.5 cm-wide dishes.

3.2.2. Step 1: Ambient pressure experiences setup and methods

The different phases of the work required the application of different experimental conditions and the acquisition of various types of experimental data. The original setup designed for this work is schematized in figure 3.3, while its implementation is presented in figure 3.4.

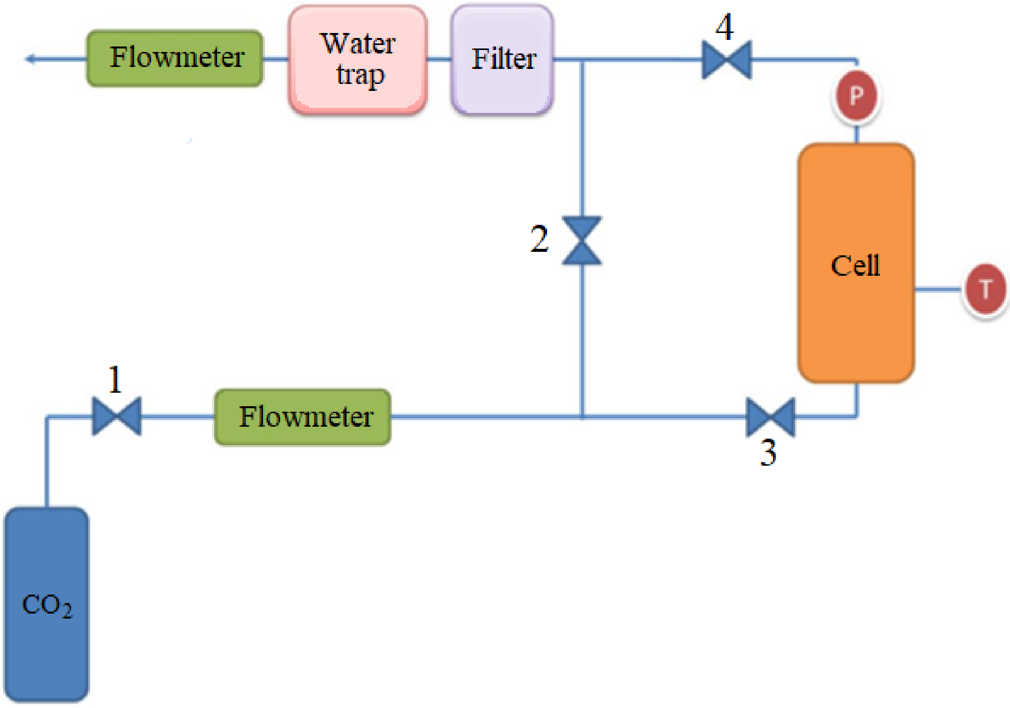


Figure 3.3: Scheme of the original setup.


Figure 3.4: Implementation of the original setup.

The experimental system presented consists of a cylindrical stainless-steel cell with a volume of 300 mL (0.3 L) at the inlet and outlet of which are connected to two flowmeters that allow to measure the CO_2 volume flow rate entering and leaving the cell.

The first flowmeter is a *DPC precision digital mass flow controller with multi gas functionality*, supplied by *Aalborg*. It can simultaneously display mass flow, volumetric flow, pressure, and temperature, and which not only allows to measure the gas flow entering the cell, but also and more importantly provide accurate and stable control of the flow rate. Therefore, this instrument corresponds to both the first flowmeter schematized in figure 3.3, and the valve that precedes it (valve 1), which corresponds to the DPC control system.

The second flowmeter is a DPM *multi parameter - multi gas mass flow meter*, supplied by *Aalborg*. This flowmeter can provide accurate measurements of mass flow rate, volumetric flow rate, pressure, and temperature of process gases. It doesn't allow to control the flowrate; therefore, it is just a measuring device.

The cell is equipped with a system for the instantaneous temperature measurement, which consists of a type K thermocouple and a piezoresistive pressure transmitter for the pressure measurement. The pressure transmitter can only work in the in the 0-2 bar pressure range.

Between the cell and the second flowmeter there are two other devices: a water trap which allows to filter any water present in the stream leaving the cell and a filter for solid particles. Both devices are used to avoid damaging the second flowmeter which is particularly sensitive to the presence of water or solid particles.

The stainless-steel connections between the various elements of the experimental system allow to make a by-pass, directing the flow from the first flowmeter to the second flowmeter without passing through the experimental cell. The by-pass can be realized thanks to the presence of three ball valves that in the diagram in figure 3.3 correspond to the valves 2, 3 and 4. Valves 3 and 4 allow also to isolate the experimental cell and therefore to perform a closed-system experiment, which is particularly important in the thermodynamic equilibrium – pressure monitoring phase.

The various measuring devices, namely the two flow meters, the thermocouple, and the pressure transmitter have been connected to a DL7 multichannel electronic data logger, which allows to display the measured values and to collect and extrapolate the experimental data.

The 300 ml stainless steel cell described above presents some practical problems: the particularly small volume does not allow the insertion of samples with an appreciable mass, as will be explained in detail below, this work is carried out on materials in which it is possible to solubilize very limited amounts of carbon dioxide when compared for example with the quantities that are adsorbed by the most known adsorbent materials (e.g., activated carbon). In addition, regardless of the volume itself, it is possible to insert the samples inside the cell through two very small circular openings, with a diameter of 1 cm. Although it is possible to insert within this cell the asphalt mix (it is a granular material) without any problems, it is particularly difficult to insert any bitumen samples. In theory it would be possible to insert small pieces of bitumen less than one centimeter, but the recovery of such samples and in general the cleaning of the cell would be very difficult. In addition, as it is explained in paragraph 3.2.1, bitumen samples are made in the form of thin 8.5 cm of diameter circular layers, making this device incompatible with samples realized in this form. The 300 ml stainless steel cylinder was however used for experiments involving pressure monitoring and the achievement of equilibrium pressure, as it makes it possible to ensure tightness at weak pressures and thus to provide valid experimental data.

To allow the use of samples with greater mass and with the required characteristics (thin circular layers for the bitumen samples), a second larger experimental cell has been built, replacing the 300 ml stainless steel cylinder in the experimental setup. This second cell is shown in figure 3.5. This experimental cell consists of a cylindrical plexiglass shell with a diameter of

10 cm and height of 15 cm, which is placed between two stainless steel bases, also cylindrical. The seal between the plexiglass shell and the lower base is made by using a silicone sealant, and between the shell and the upper base by using a rubber gasket and three threaded rods (and three nuts) which provide compression. This cell is connected to the other elements of the experimental setup by two rubber tubes.

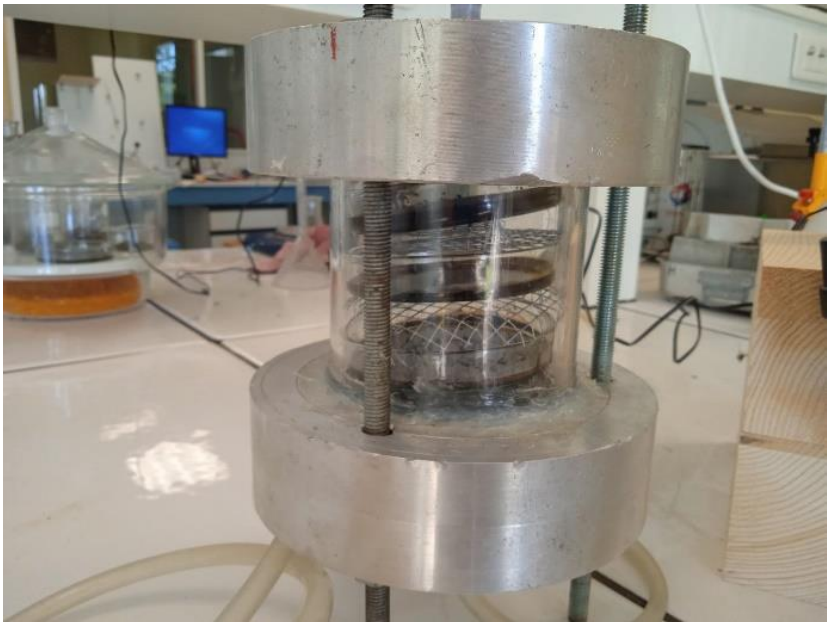


Figure 3.5: Larger experimental cell in plexiglass with two stainless steel bases.

The gravimetric analysis of the samples has been carried out using a precision scale with a resolution of 10^{-4} g.

The chosen method to characterize the CO_2 solubilization process in bitumen is a gravimetric method, which consists of carefully measuring the mass of the samples before and after being inserted in the experimental cell for a certain amount of time (several days – more than one week for each experience in this phase) where there is a volume consisting exclusively of carbon dioxide.

In the procedure initially planned for this work, the evaluation of the process of solubilization of carbon dioxide in the materials analyzed had to be done by means of a volume flowrate differential analysis of the CO_2 entering and leaving the cell. This method consists in inserting the material inside the carbonation column and sending a constant flow of CO_2, to saturate the column interior with an atmosphere of carbon dioxide. The measure of the outgoing flow compared with the incoming flow would in theory allow to calculate the difference in terms of the volumetric flow rate, and then easily calculate the carbon dioxide retained by the sample and the kinetics of the process.

This method applied to the investigated materials did not lead to any appreciable result, as the outgoing flow rate in the case of cell with the sample did not show substantial differences with the empty cell one, or very small differences, attributable to experimental error fluctuations, making the characterization of the process impossible. The same method as applied to a NC60 active carbon sample, for which non-negligeable differences between the inlet and outlet flowrate have been observed, thus confirming the validity of the experimental method.

In other words, the process of solubilization/adsorption of carbon dioxide in these materials has a particularly slow kinetics, and the amounts retained by these materials seem to be very small. These two factors combined do not allow to characterize this phenomenon through the comparison of volumetric flow rates, making this method not compatible with the materials analyzed, forcing to select the gravimetric technique described above.

The mass of the samples is measured by means of a balance which is located outside the experimental cell. Therefore, to measure the mass variation it was necessary to pull out the samples from the cell. This type of ex-situ measure may not be practical because to take samples from the cell it is necessary to open it, varying the experimental conditions inside and having to wait to restore them when the samples are placed in the cell after the measurement.

This can be problematic when trying to construct a diffused CO_2-time curve to characterize the kinetics of the process, however, in this first phase the experimental conditions do not require the cell pressurization, therefore taking samples for measuring them does not demand long time and it does not disturb the experimental conditions significantly, as it is explained in paragraph 4.1.1 and shown in figure 4.2.

The experience of characterizing the mass variation by direct measurement was done on samples inserted in an experimental cell connected to an inlet flowmeter and an outlet flowmeter, and therefore subject to a constant flow of carbon dioxide of 10 ml/min. The constant exchange of carbon dioxide in the cell allows to have an atmosphere in the cell with constant characteristics, therefore, the CO_2 concentration at the bitumen-atmosphere interface can be considered constant. The temperature conditions can be also considered constant: in the room in which the tests were carried out, the temperature recorded varied between 19 °C and 21.5 °C.

3.2.3. Step 2: Higher pressures experiences setup and methods

The second step of this work, which requires higher pressures and temperatures, has been carried out by utilizing another type of vessel: the 7.6 L stainless steel vessel supplied by *Parr instruments*. This device (*series 4666*) has a maximum working pressure of 130 bar and a maximum working temperature of 350 °C, values far beyond those associated with this investigation, thus allowing to carry out these experiments safely. The size and technical characteristics of this vessel are summarized in table 3.1, and a scheme is reported in figure 3.6.

Table 3.1: Technical characteristics of the 4666 Parr Vessel.

Model	4666
Size	7.99 L
Head style	VGR, Thermowell
Maximum Working Pressure	1900 psi (131 bar)
Maximum Working Temperature	350 °C

This vessel is provided with a 1000 psi (68 bar) pressure gauge. Although it is possible at any time to visualize the pressure inside the device, it is not possible to record its variation over time and in general it is not easy to appreciate any pressure variations related to adsorption/absorption phenomena as it would be by using a digital pressure gauge or more generally a gauge with a higher resolution. For this reason, the samples mass variation is the only method used at this stage to characterize the CO_2 solubilization phenomenon.

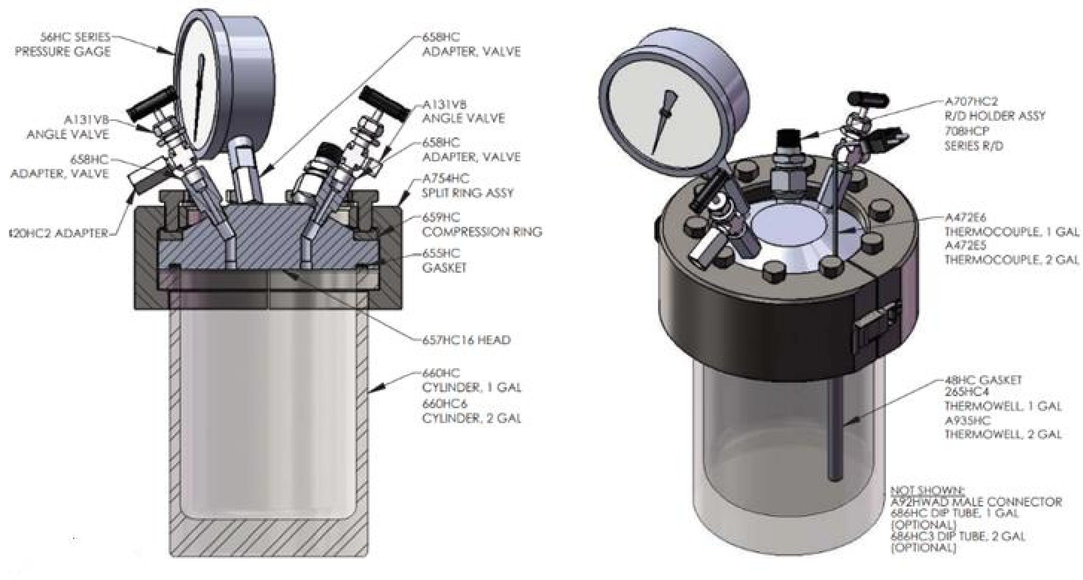


Figure 3.6: Scheme of the 4666 Parr Vessel, from [41].

3.2.4. Step 3: Gas Chromatography experiences setup and methods

For the temperature variation step, the vessel is provided with a heating system associated with a control system. The heating system consists of an oven in the shape of a cylindrical shell that is placed around the vessel, as a jacketed system. The oven works thanks to an electric power supply. The heating system is then connected to the control system, which in turn is connected to a temperature measurement system (a thermocouple) inserted in a special section inside the vessel. The heating system together with the control system is shown in figure 3.7.

Figure 3.7: Heating system: cylindrical shell oven (right) connected to the control system (left).

The gas phase chromatography analysis has been carried out in a *PerkinElmer Clarus® 590 Gas Chromatograph* (GC), which is a fully automated gas chromatograph. All instrument functions are set up and monitored through a touch screen. The intuitive graphical user interface includes a real-time chromatogram display.

The *PerkinElmer Clarus® 590 Gas Chromatograph* (GC) is shown in figure 3.8.

Figure 3.8: PerkinElmer Clarus® 590 Gas Chromatograph (GC).

To analyze the components released from samples following the heating process, a sample of the atmosphere within the headspace of the Parr reactor was taken and stored within the *Tedlar® Gas Sampling bags*, which are provided with a *Thermogreen® polymer LB-2 Septa*, which ensure bags sturdy and leak-proof under most demanding sample conditions. The Tedlar film can be exposed to temperatures up to 204°C, making it compatible with the experimental conditions, for which the sampled gas reaches temperatures up to 160°C. Figure 3.9 shows some *Tedlar® gas sampling bags* with different samples from the last phase of the work.

Figure 3.9: Tedlar® Gas Sampling bags with different bitumen fumes samples.

In order to transfer the components to analyze in the injector port of the gas chromatograph, a *Supelco Solid Phase MicroExtraction Fiber Holder* has been used, which allows to perform the Solid Phase MicroExtraction (SPME) technique, which is an extraction technique for organic compounds in which the analytes are adsorbed directly from the samples onto a fused-silica fiber that is coated with an appropriate stationary phase until equilibrium is reached [50]. The fiber is then inserted into the injector port of the chromatograph where it is heated, and the analytes are rapidly thermally desorbed into a capillary GC column for analysis.

The first phase of this third experimental step consisted in obtaining the samples to be analyzed with the gas phase chromatography. These samples consist of the gaseous volatile components released by the materials under study when heated to temperatures of up to 160 °C.

The bitumen samples were first subjected to a carbonation process, inserting them for one week (168 hours) inside the Parr reactor in which a CO_2 atmosphere was introduced, with a pressure slightly higher than the atmospheric pressure and at room temperature.

Then, at the end of the carbonation phase at room temperature, the reactor has been placed inside the heating oven shell, connected to the temperature controller. At this point the heating system has been switched on. The reactor and its contents have been heated to five increasing temperatures following a step procedure (80 °C, 100°C, 120°C, 140°C and 160 °C). Each time the reactor reached one of the five temperatures at which the characterization was to be carried out, the system maintained this temperature for 10 minutes, after which a sample of the gaseous atmosphere in the reactor was taken.

To collect and store a sample of the atmosphere in the reactor at each of the five temperatures, a gas sampling bag was used. The gas sampling bag has been connected to one of the two outlets of the reactor by means of a stainless-steel connection that assured the airtight seal with the bag valve. The oven-reactor-bag system is shown in figure 3.10.

Figure 3.10: Oven-reactor-bag system for the collect of the bitumen fumes samples.

Five samples in five sampling bags corresponding to the five temperatures listed above have been collected. To subject the contents of the bags to phase chromatography gas analysis, an instrument had to be used to allow the transfer of the analytes of each sample from the bag to the chromatograph injector unit. A solid phase microextraction technique (SPME) has been performed, by using a fused-silica fiber inserted in a specific fiber holder. For each analysis the fiber has been exposed to the gas inside the bag for about 30 minutes. Figure 3.11 shows how the fiber has been exposed to the bags content. Then the fiber has been inserted into the injector port of the chromatograph, where the heating allowed to rapidly desorbs the analytes into the capillary column of the chromatograph for the analysis.

Figure 3.11: Solid phase microextraction technique: fiber exposed to the gaseous analytes to be adsorbed.

The temperature program used for the GPC analysis is based on the program of Sutter et Al. [51] described in paragraph 2.7. The program described in the report has an intermediate phase with a particularly high T gradient of 100 °C/min. With the chromatograph available, however, it is possible to apply a maximal gradient of 45 °C/min, and therefore the temperature program of this work is "delayed" compared to the one described in the technical report. A comparison of the two programs is presented in figure 3.12.

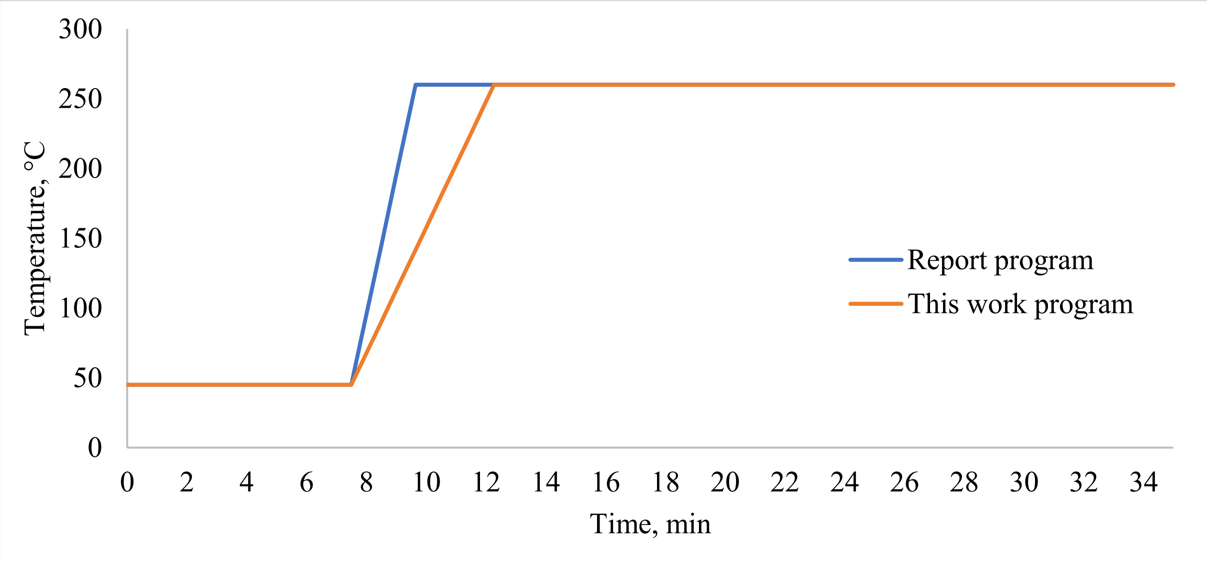


Figure 3.12: Comparison between the program of Sutter et Al. [51] and the selectable program executed in this work.

4. Results

4.1. Step 1: Ambient pressure experiences

4.1.1. Mass variation analysis

The results of this first phase at ambient and free-flow conditions are presented in Figure 4.1. The figure shows the CO_2 mass fraction after 168 hours in a cell with a CO_2 atmosphere at a constant ambient pressure (there is no difference in terms of pressure inside and outside the cell). The results are presented as mean values, and the experimental values obtained fall within the error bar shown in the graph for each point, which represents the experimental range (min-max values).

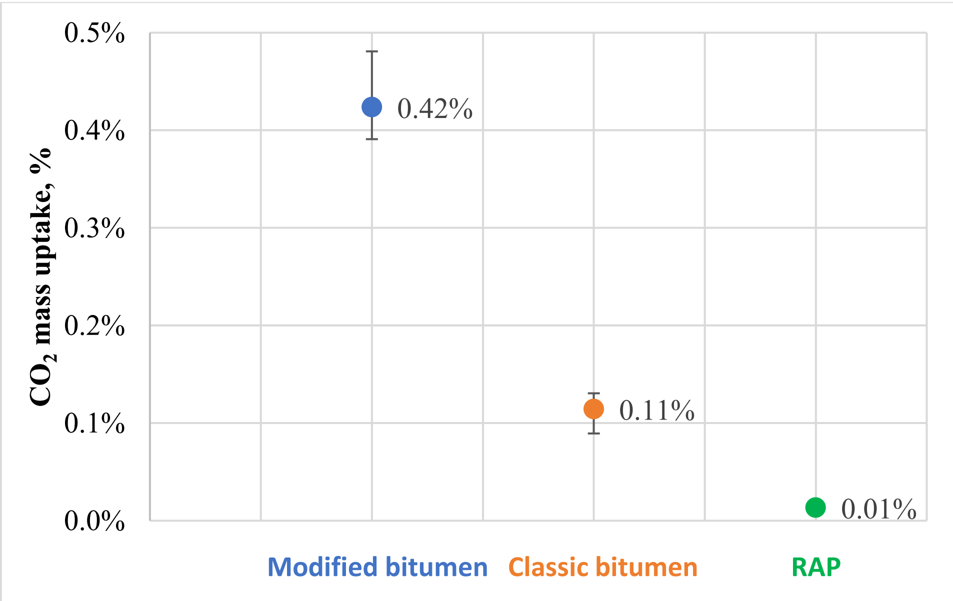


Figure 4.1: CO_2 mass uptake (%) after 168 hours in a cell with a CO_2 atmosphere at a constant ambient pressure.

The values are represented in terms of mass uptake percentage, which indicates the percentage increase that the sample has undergone during the exposure to carbon dioxide, or, in other words, the maximum amount of CO_2 that each sample can hold expressed as a percentage fraction of the mass of the sample.

It is not possible to make a direct comparison between this work experimental data and those of other works because, as already extensively discussed during the presentation of the bibliographic panorama on this topic, the characterization of the solubility of carbon dioxide in these materials at ambient temperature and pressure conditions has not been carried out.

What can be highlight is the difference in terms of maximum CO_2 uptake between the three materials investigated: although the amounts of absorbed CO_2 are quite small in absolute terms, modified bitumen has a maximum capacity of about four times that of unmodified bitumen.

Another interesting element is the particularly low amount of CO_2 adsorbed by RAP (asphalt aggregate). In fact, this material can adsorb slightly more CO_2 than 0.01% of its mass, an amount so low that it excludes any hypothesis of practical application of this process.

Nevertheless, it would be more correct to calculate the percentage variation, not based on the total weight of the sample, but based on the bituminous fraction, thus excluding from the calculation the mass of the various inert components.

Moreover, it is possible to compare the percent mass uptake value obtained in this work for the classic bitumen formulation under room temperature and pressure, with the results of other works at room temperature but higher pressures. The value obtained in this work, about 0.1%, is significantly lower than the one obtained by Mehrotra and Svrcek [35], in which a sample of *Cold Lake Bitumen* absorbs about 3% of its mass at 26°C and 20 bar. This value is also lower than the one obtained by Apeagyei and Airey [2], which is about 0.3% - 0.4%: it is of the same order of magnitude, because it has been realized at 20°C and only 2.75 bar.

Figure 4.2 compares the average of the results of experiments carried out leaving samples for 168 hours without carrying out intermediate weighing, and the average of the results of experiments for which samples have been taken several times for kinetic characterization.

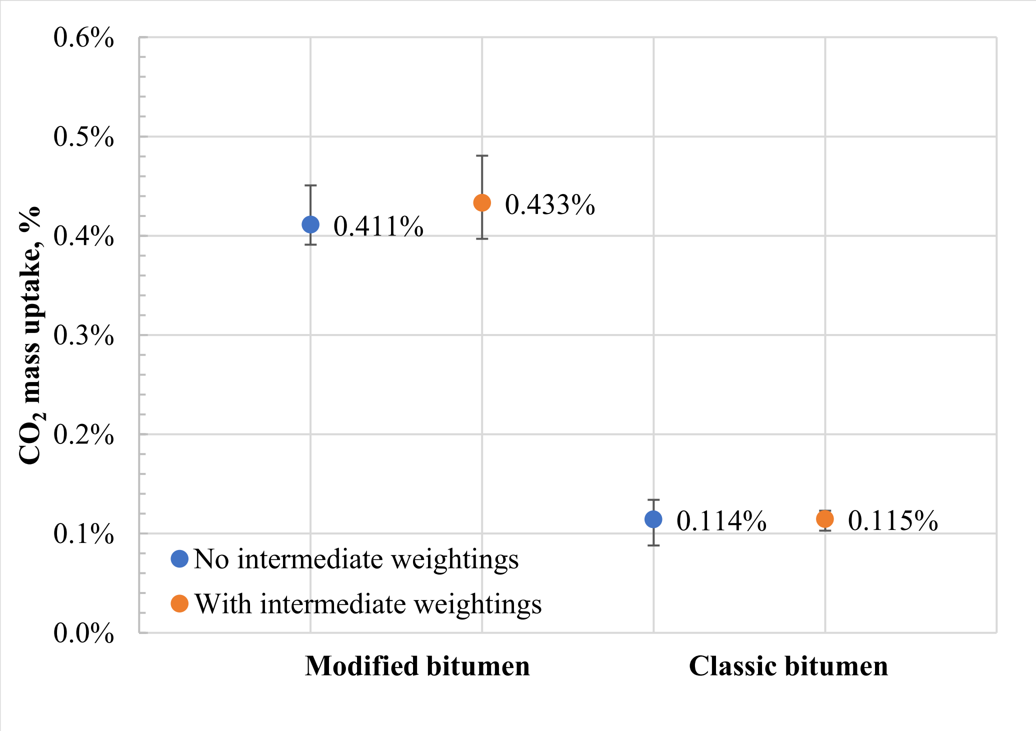


Figure 4.2: comparison between the average of the results of experiments carried out without carrying out intermediate weighing, and the average of the results of experiments for which samples have been weighed several times for kinetic characterization.

The figures do not show RAP data as all experiments with this material were not carried out including intermediate weightings. The amount of CO_2 that the RAP adsorbed is so low that it was not possible to realize the tracing of its mass uptake/time curve, as the act of taking the sample from the cell several times disturbed the adsorption process, eventually resulting in inconclusive data.

On the other hand, the average values associated with the two types of bitumen are very close independently of the procedure used (single experiment without intermediate samples or experiment with different intermediate weightings), showing that for these materials the act of taking samples for a few seconds to be able to evaluate the mass, does not particularly disturb the reliability of the experimental results and still allows to correctly characterize the process.

4.1.2. Characterization of the solubilization kinetics

The kinetics of the solubilization process were characterized by recording the masses several times during the duration of the whole experiment and plotting the CO_2 mass uptake as a function of time. This procedure has been applied to different samples of both type of bitumen (modified and unmodified). As already explained in the previous paragraph it was not possible to perform the same type of characterization for asphalt aggregates (RAP), as the handling of samples for weighing led to inconclusive results, probably due to the fact that the amount adsorbed a few hours of exposure to the atmosphere of carbon dioxide is very low (a fraction of the already quite low values for 168 hours of continuous exposure, which as illustrated in the previous paragraph has been found to be around 0.01%), so low that it is likely to be of the same order of magnitude as the measurement error, and for which even minimal desorption has negative effects on the quality of the adsorption characterization process.

Figures from 4.3 to 4.6 show the evolution over time of the CO_2 uptake expressed as mass percentage for modified bitumen and classic bitumen respectively. Figures 4.3 and 4.5 show the experimental points of each sample for the two bitumen formulations, highlighting that there is certain variability between the various samples, which have different maximum capacity values within a certain range. After 168 hours of direct exposition to a CO_2 atmosphere at atmospheric pressure, modified bitumen's mass uptake is between 0.39% and 0.47% (with an average value of 0.431%), while unmodified bitumen's mass uptake is between 0.10% and 0.13% (average value 0.115%).

This variability, which is linked to the error bars associated with the maximum capacities of the various samples in Figure 4.1, can be explained by a whole series of factors that could not be controlled during the experience, first and more importantly, the temperature of the room where the experimental system was present, but also the small variations in mass of the samples or the position of the same inside the cell.

The process of CO_2 solubilization in both bitumen formulations follows a saturation pattern, this means that the process starts with a certain kinetics that slows progressively until the CO_2 uptake reaches a certain value for which the kinetics becomes zero and the process of solubilization stops. In graphical terms the slowing of the kinetics of the solubilization process translates into a curve that grows more and more slowly until it reaches the maximum capacity value.

A clear difference between the curves of the two formulations is that the curve associated with unmodified bitumen grows steeper at the beginning and reaches the maximum capacity value earlier. In contrast, the curves associated with modified bitumen, although they reach higher absolute values, grow less steeply.

In both cases the uptake values after 168 hours (one week) from the start of the experiment could be considered as maximum capacity values. To verify that the uptake after 168 hours can be considered the maximum uptake value, some samples were left for a longer time, up to 216 hours: what has been observed that can be seen in both figures 4.3 and 4.5 is the confirmation that for both formulations the curves do not grow considerably after 168 hours, thus the values at 168 h can be considered the maximal values. This is true especially for the unmodified bitumen, while bitumen modified has a slight increase of 0.01% between 168 hours and 216 hours.

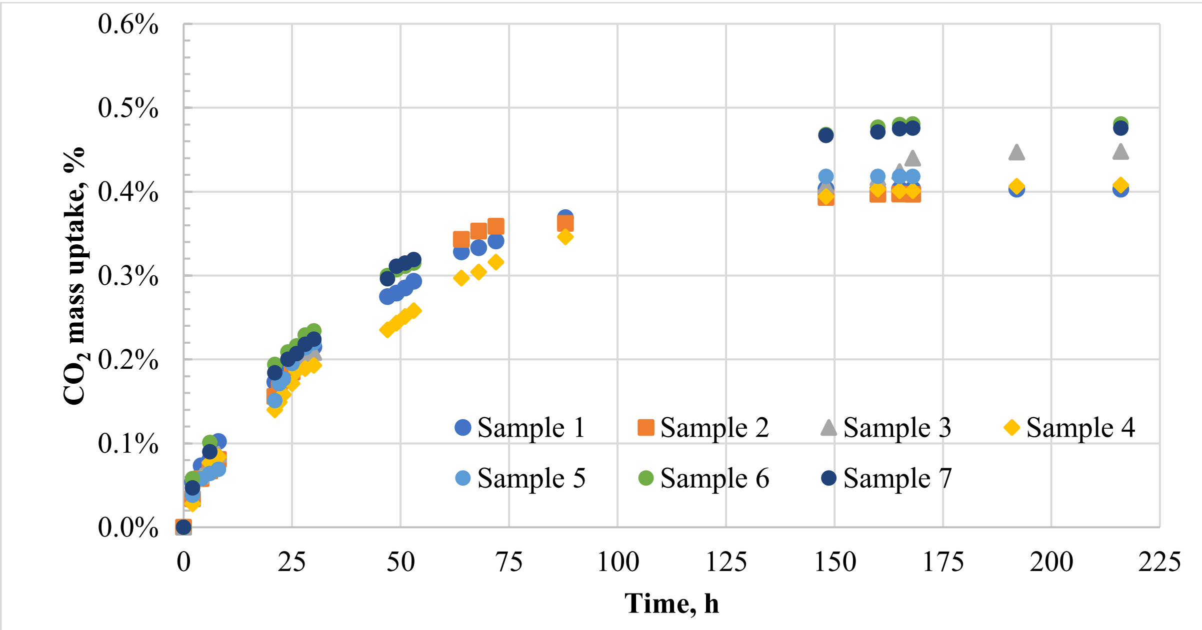


Figure 4.3: CO_2 uptake expressed as mass percentage as a function of time (number of hours passed since the start of the experiment) for modified bitumen. Experimental points of each sample.

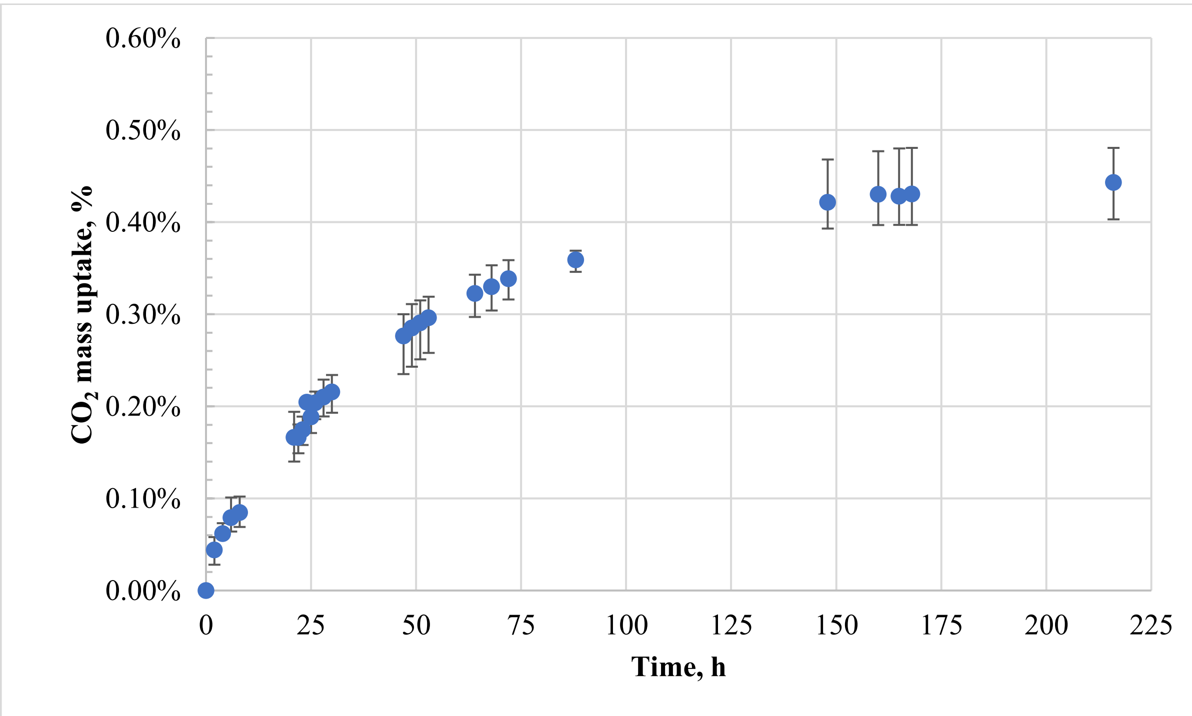


Figure 4.4: CO_2 uptake expressed as mass percentage as a function of time (number of hours passed since the start of the experiment) for modified bitumen. Average experimental points with min-max values bars.

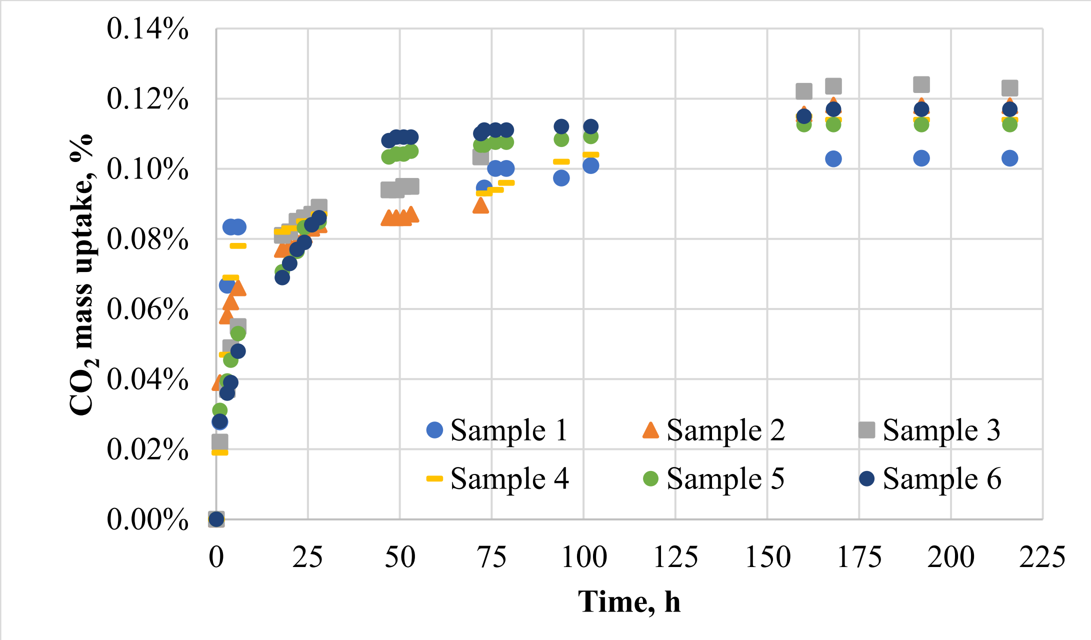


Figure 4.5: CO_2 uptake expressed as mass percentage as a function of time (number of hours passed since the start of the experiment) for classic bitumen. Experimental points of each sample.

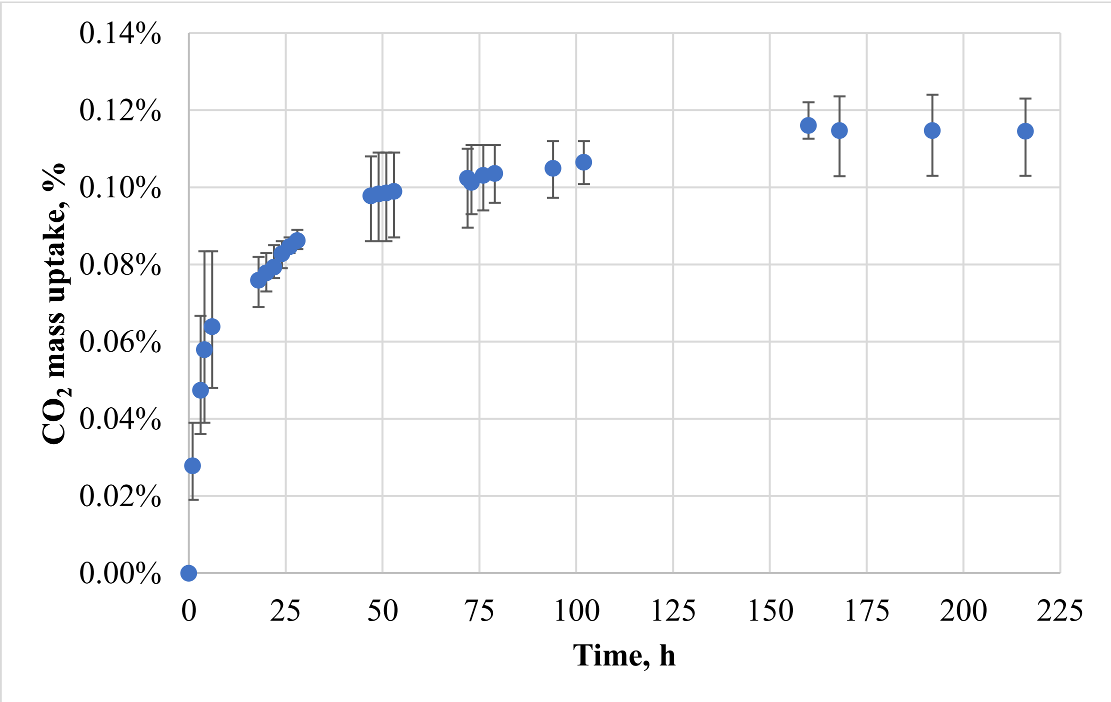


Figure 4.6: CO_2 uptake expressed as mass percentage as a function of time (number of hours passed since the start of the experiment) for classic bitumen. Average experimental points with min-max values bars.

With the data at disposal, it is possible to model the CO_2 solubilization/diffusion kinetics. The Peleg model has been selected, which was applied to model this process by Apeagyei et Al. [2], one of the works used as a reference for this work. The experimental data (mass uptake and time) have been fitted to a two-parameter non-exponential empirical model originally proposed by Peleg (1988) for moisture diffusion in foods. The Peleg model shown in equation

2.5 and 2.6 enables prediction of moisture uptake after a long exposure from experimental data obtained in relatively short time. The model has been found to model moisture diffusion in bituminous mixtures very well (Apeagyei et al., 2013). This model has been successfully used in Apeagyei's work to predict CO_2 solubilization too.

To find the model's parameters, it is necessary to linearize the equation. There are four different ways to linearize this equation, as showed in table 4.1.

Table 4.1: Possible ways to linearize the Peleg model equation.

Linearization	Equation
1	$\frac{t}{x} = C_1 + C_2 t$
2	$\frac{1}{x} = \frac{C_1}{t} + C_2$
3	$\frac{x}{t} = -\frac{C_2}{C_1} x + \frac{1}{C_1}$
4	$x = -\frac{C_1}{C_2} \frac{x}{t} + \frac{1}{C_2}$

All the presented parameters for the four possible linearization are presented in table 4.2 for the modified bitumen and in table 4.3 for the unmodified bitumen, together with the coefficient of determination of the linearization, the statistical parameter RSQ which is used to evaluate the quality of the model, this parameter is the square of the *Pearson correlation coefficient*, which is the ratio between the covariance of the two variables and the product of their standard deviations, as indicated by equation 4.1.

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2}\sqrt{\sum_{i=1}^{n}(y_i - \bar{y})^2}} \quad (4.1)$$

where n is experimental points number, x_i is the n_i measure value, y_i is the corresponding predicted value, $\bar{x}$ and $\bar{y}$ are the measures and the predicted values averages respectively.

Table 4.2: Peleg model parameters for all four possible linearisations for modified bitumen.

Linearization	C_1, h	C_2	k, h^{-1}	x_e	RSQ
1	7576.013	189.393	**4.735**	**0.528%**	**99.419%**
2	4485.057	296.672	19.624	0.337%	90.939%
3	6475.669	209.332	6.767	0.478%	98.313%
4	5658.653	231.750	9.941	0.431%	96.543%

Table 4.3: Peleg model parameters for all four possible linearisations for classic bitumen.

Linearization	C_1, h	C_2	k, h^{-1}	x_e	RSQ
1	7780.874	839.447	**90.565**	**0.119%**	**95.887%**
2	2734.372	989.308	357.936	0.101%	92.090%
3	3558.719	931.694	243.923	0.107%	94.138%
4	3088.170	956.023	295.962	0.105%	93.189%

As it can be clearly seen by observing the RSQ values, the first linearization allows to find the model's parameters that produce the best quality model. The model built with these parameters is showed together with the experimental points in figure 4.7 (modified bitumen) and in figure 4.8 (classic bitumen).

In general, this type of model seems to provide quality modelling especially in the case of modified bitumen, for which the coefficient of determination is equal to 99.42%. According to the model, the maximum value for the CO_2 uptake would be on average 0.528%. This would mean that modified bitumen could still absorb a considerable amount of CO_2, but it would take a particularly long time to do so, as the model predicts that only after about 720 hours (one month) the sample would reach an uptake of 50% and only after 2600 hours (three months and a half) an uptake of 52%.

As regards the model associated with unmodified bitumen, the model foresees a maximum capacity of 0.119%, very close to the average observed value of 0.115%, indicating that this bitumen formulation has practically reached the maximum solubilization limit. Moreover, in this case the process kinetics is faster, as the sample reaches values close to the maximum capacity in a much smaller time than that used by the modified bitumen, in other words the curve grows very quickly in the first moments of the process, and this is mathematically showed in the k value, which is about 90 h^{-1}, while in the case of modified bitumen it was around 5 h^{-1}.

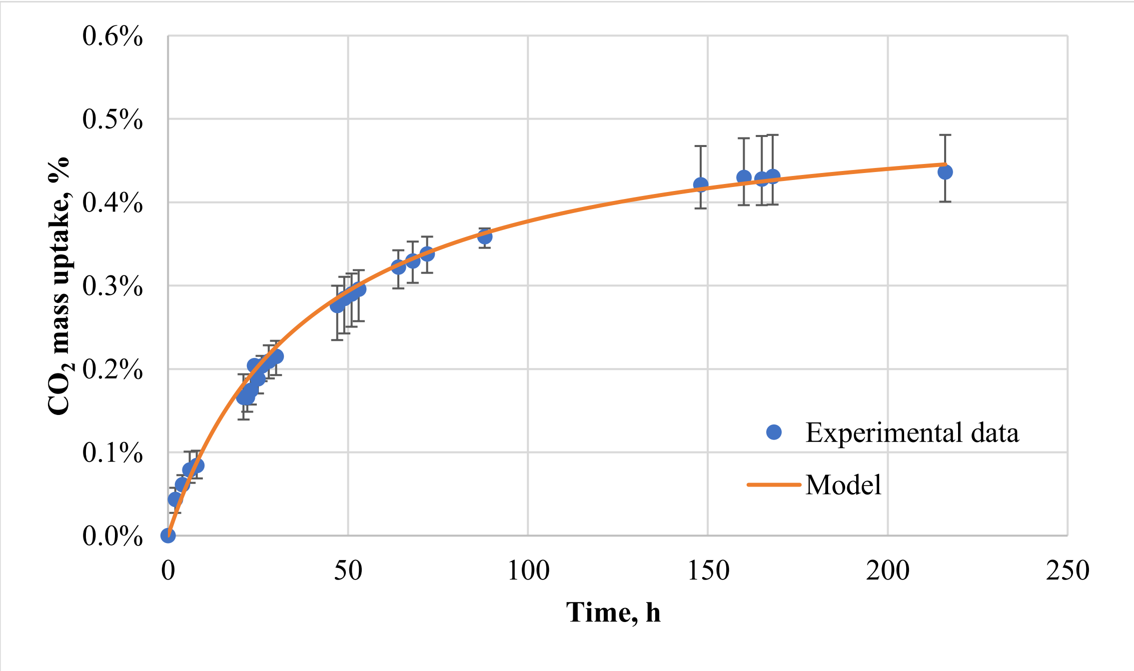


Figure 4.7: Peleg model (orange line) compared with experimental points (blue points), modified bitumen results.

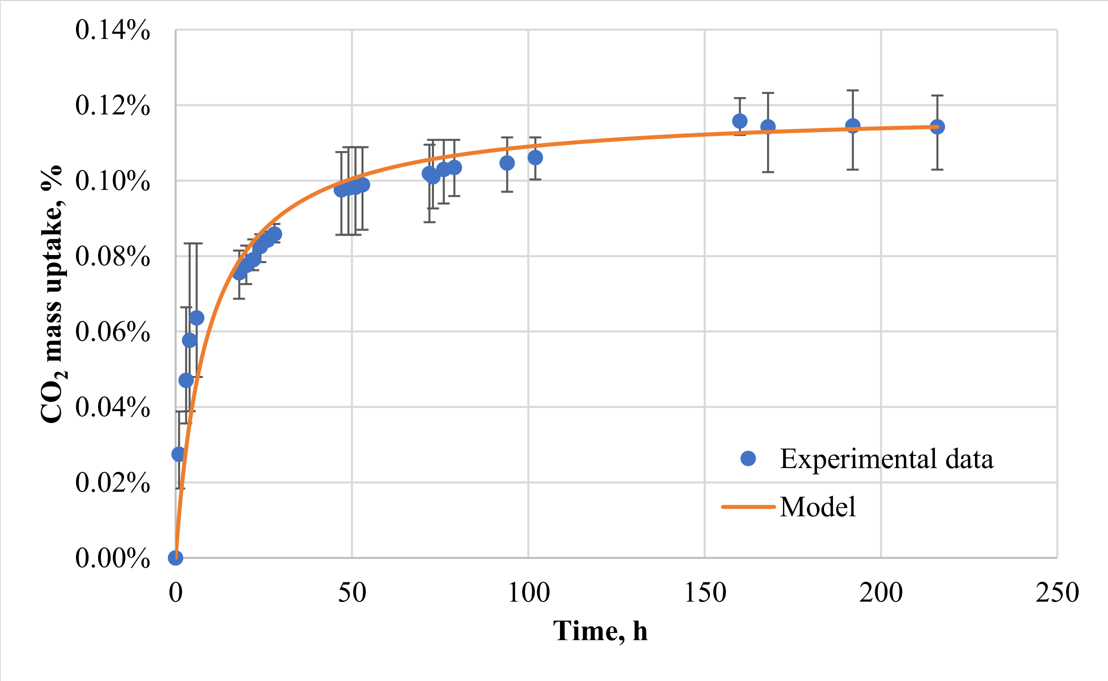


Figure 4.8: Peleg model (orange line) compared with experimental points (blue points), classic bitumen results.

4.1.3. Characterization of the CO_2 release kinetics

Most of the samples that have been utilized to characterize the diffusion/adsorption process in the two bitumen formulations and in the asphalt aggregates, have been also used to characterize the opposite process, the gradual release of diffuse or adsorbed CO_2 when the samples are exposed to the atmosphere (free air at room temperature and pressure). As soon as the samples are taken from the experimental cell and after being weighed, they are placed in a cylindrical container with an opening on the top that allows communication with the external atmosphere and air exchange. Samples are not simply placed outside in order to prevent contamination by external material, such as dust. In the container a certain amount of hygroscopic material (such as silica gel) is inserted to keep the moisture content inside the container low, and to avoid the possibility that water condenses on the samples corrupting the measuring process.

The mass of the samples is then measured progressively. What was observed for both bitumen formulations is a decrease in sample mass due to desorption of solubilized CO_2.

Figure 4.9 shows, for example, the release curve of a particular modified bitumen sample. The sample just taken from the cell after the solubilization process presents a CO_2 uptake of 0.397%, and after 216 hours (9 days) of exposure to free air the CO_2 uptake comes down to 0.315%. This means that the sample lost 21% of the CO_2 it had absorbed, retaining 79%. Similarly, the desorption curve of a classic bitumen sample is shown in figure 4.10 as an example: this sample at the beginning presents a CO_2 uptake of 0.103% and after 216 hours it comes down to 0.035%, losing about 76% of the original value and retaining only 36%.

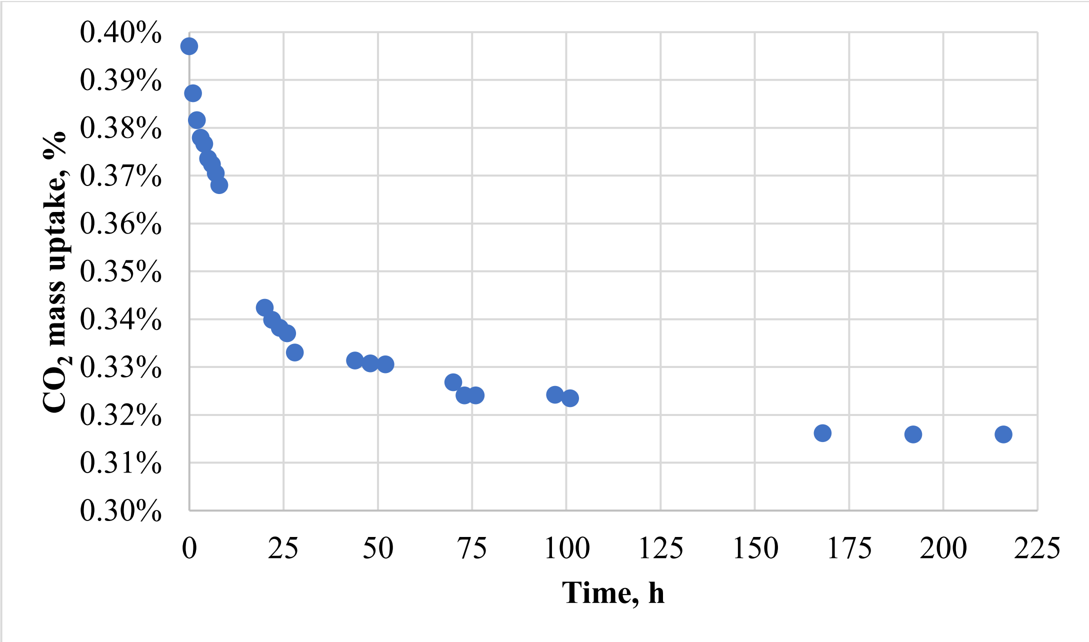


Figure 4.9: CO_2 mass uptake in modified bitumen during the release phase (sample exposed to free air).

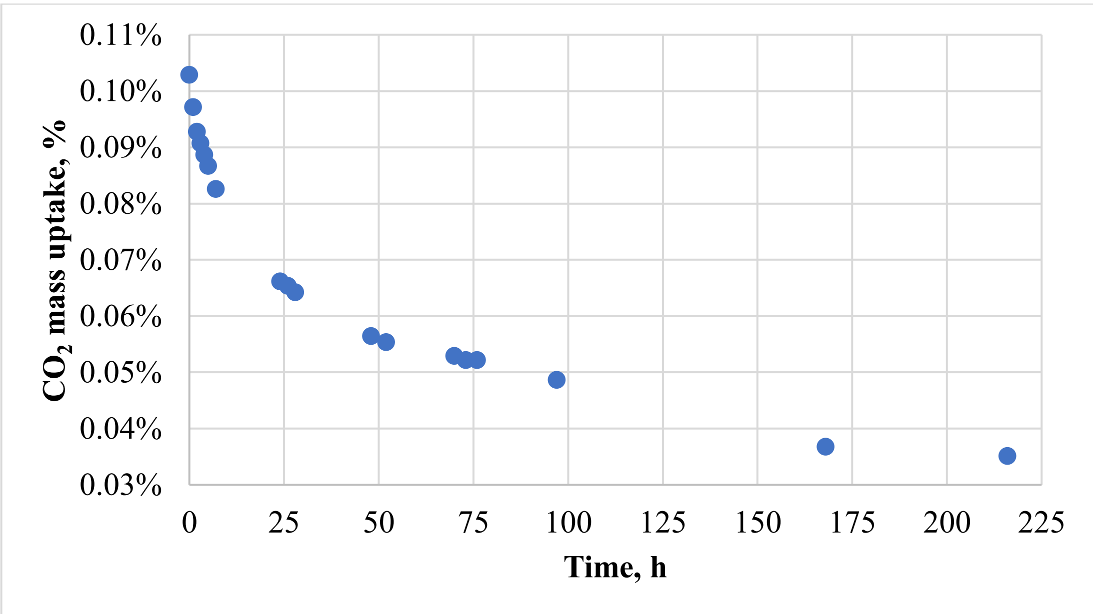


Figure 4.10: CO_2 mass uptake in classic bitumen during the release phase (sample exposed to free air).

To characterize the average behavior of each bitumen formulation, the amount of retained CO_2 as a fraction of the starting value (at the beginning of the release process) is plotted, in such a way the curves start at 100% (the initial value corresponding to the maximum uptake of CO_2) and ends at a final equilibrium value corresponding to the initial amount fraction that the sample retains after 216 hours. These plots can be seen in figures 4.11 and 4.12 for modified bitumen and classic bitumen respectively.

As can be seen in Figure 4.11, in the case of modified bitumen the amount retained after 216 hours is on average 79%. Considering that the mean mass uptake value after 168 h for this material is 0.43 ± 0.04 %, after 9 days of air exposure the sample is able to retain between

0.32% and 0.39% of CO_2, which is more than five times the average CO_2 mass concentration in air (0.063%) [16].

On the other hand, in figure 4.12 the classic bitumen loses most of the solubilized CO_2: after 9 days, this formulation holds on average only 32% of the original amount, and since the initial amount had been calculated to be 0.115 ± 0.015 %, this means that this bitumen after more than one week retains a CO_2 concentration smaller than that the air's one.

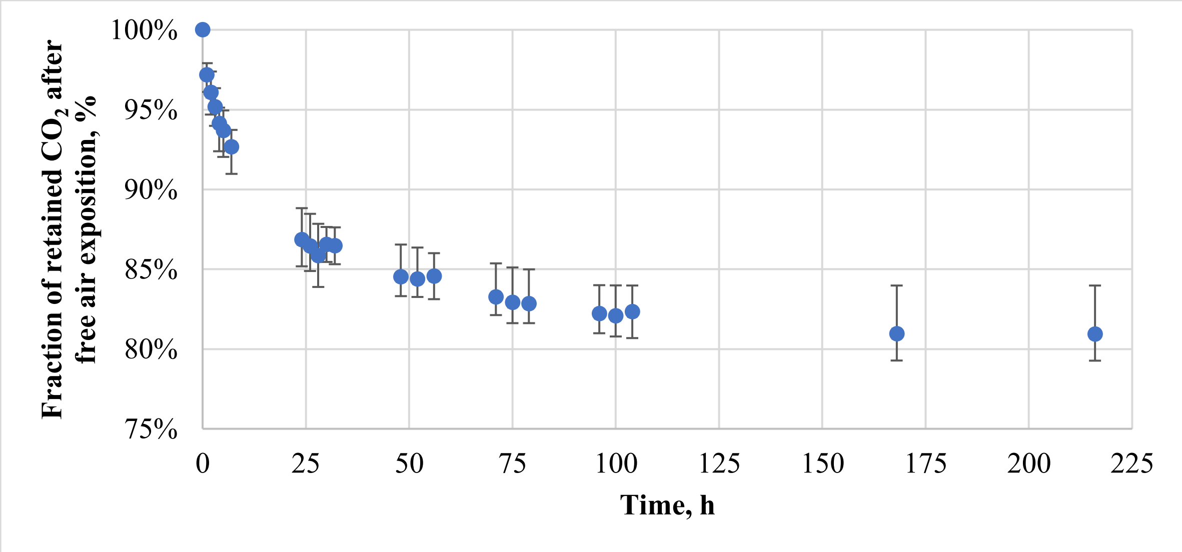


Figure 4.11: Fraction of retained CO_2 in modified bitumen during free air exposition, expressed as percentage of the maximal solubilization value achieved after 168 hours of carbonation. The points indicate mean values, the min-max range is expressed by the bars.

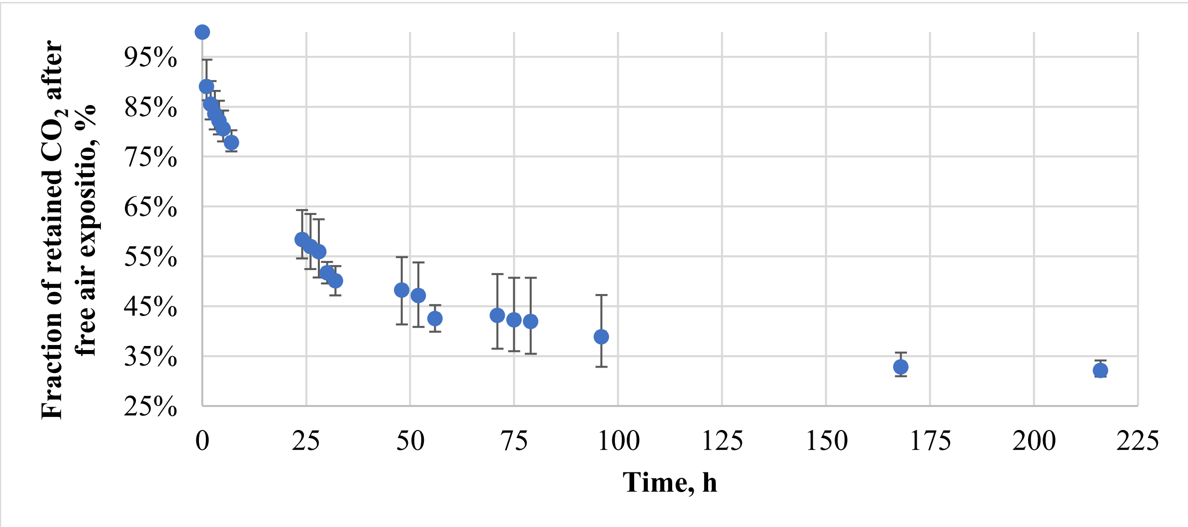


Figure 4.12: Fraction of retained CO_2 in classic bitumen during free air exposition, expressed as percentage of the maximal solubilization value achieved after 168 hours of carbonation. The points indicate mean values, the min-max range is expressed by the bars.

After applying an empirical model to the solubilization process, the same model could be applied to the release process, to obtain the quantitative parameters that represents the kinetics of the process and the equilibrium uptake retained by the material after long period of times at air exposure. Therefore, the same model (Peleg) has been selected because the physical process at the base of the desorption phenomenon is the same as the solubilization phenomenon, that is the diffusion of carbon dioxide in bitumen, but inverse.

Nevertheless, it was necessary to adapt the empirical equation to the basis of the model, and the expression of the parameters of the model, to obtain a model that could effectively represent the CO_2 release.

It should be noted, however, that unlike the case of the solubilization process, this model has never been applied in any prior work to the reverse process (CO_2 release), and therefore its actual effectiveness in predicting the behavior of the materials under study has no solid evidence to support it.

The CO_2 release-adapted model is described by equations 4.2 and 4.3:

$$x = 1 + \frac{t}{c_1 + c_2 \cdot t} \tag{4.2}$$

$$C_1 = \frac{1}{-k(x_e - 1)^2}; \qquad C_2 = \frac{1}{x_e - 1} \tag{4.3}$$

The parameters associated to this model for the two bitumen formulations are presented in table 4.4.

Table 4.4: Parameters of the Peleg-like model for the CO_2 release phenomenon

Type of sample	k, h^{-1}	x_e	RSQ
Modified bitumen	0.424	80.05%	99.32%
Classic bitumen	0.099	28.30%	98.45%

Figures 4.13 and 4.14 represent the experimental points of the CO_2 release process and the model curves for modified and classic bitumen respectively.

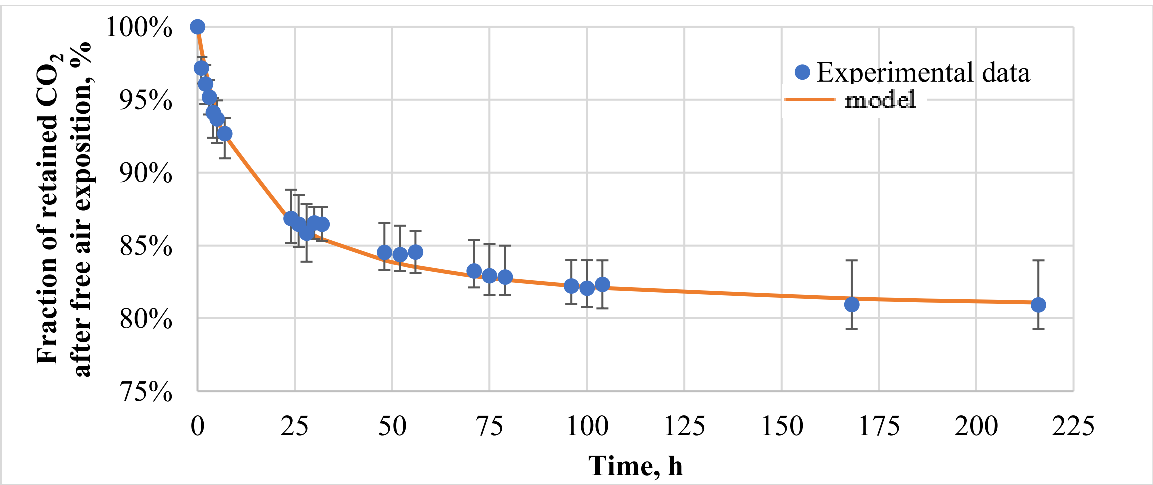


Figure 4.13: Peleg-like model (orange line) and experimental points (blue points) for the CO_2 release process of modified bitumen.

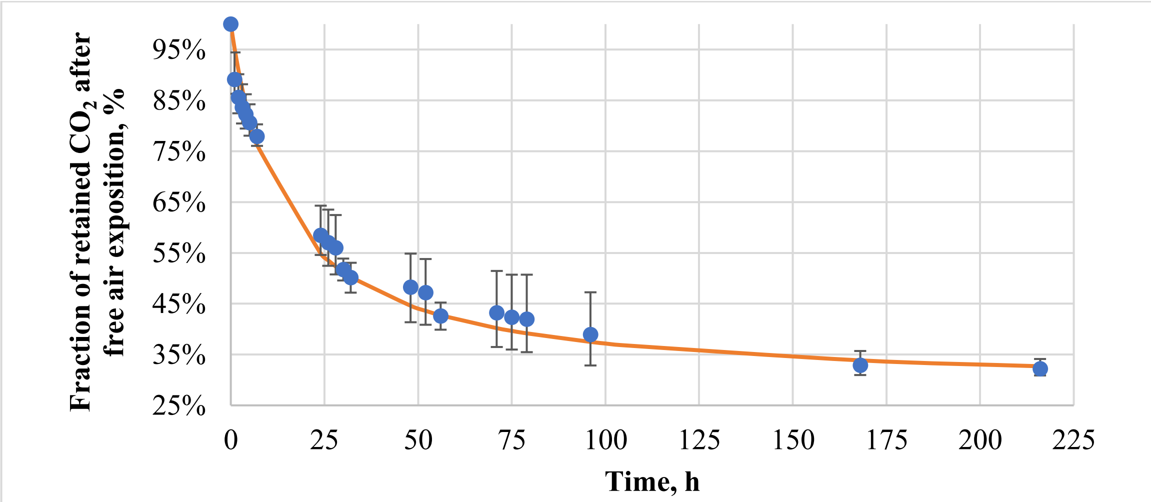


Figure 4.14: Peleg-like model (orange line) and experimental points (blue points) for the CO_2 release process of classic bitumen.

4.2. Step 2: Higher pressures experiences

4.2.1. Characterization of the CO_2 capacity after 88 hours of exposition

In this second step of this work, the CO_2 solubilization process in the materials already described in the previous chapter is described, but in this step the second device, the 7.6 L stainless steel vessel supplied by Parr instruments, is used, to characterize the process under $p > p_{amb}$ conditions. The vessel is connected to the CO_2 cylinder by a rubber or steel hose, a pressure reducer allows to adjust the cylinder outlet pressure according to the desired pressure inside the vessel. Pressures within the range 0 - 20 bar (0 - 2 Mpa) were investigated, a pressure range for which the characterization of the CO_2 solubilization in bituminous materials process is poorly developed in literature. All the experiences made in this phase were carried out at room temperature. The pressures investigated are 1.5 bar, 3 bar, 5 bar, 7 bar, 9 bar.

The selected method to characterize the CO_2 diffusion process was once more the gravimetric method, as it was not possible to monitor the pressure evolution within the vessel: pressure variations are relatively small and cannot be precisely defined by observing the pressure gauge.

At least three samples were utilized for each material for each pressure condition, in order to define the experimental variability. In each experience, the samples were placed in the vessel under the high-pressure CO_2 atmosphere for 88 hours. This means that the values found after such experiences do not correspond to the maximum capacity. This choice was made for practical reasons, to obtain as many results as possible in the time available for such experiences. One-week experiences for each pressure investigated would have reduced the number of feasible experiences and experimental data. The maximum capacity at 3 and 9 bar was however characterized, the related results will be presented in paragraph 4.2.2.

Figures 4.15, 4.16 and 4.17 show results for modified bitumen, classic bitumen, and asphalt aggregates.

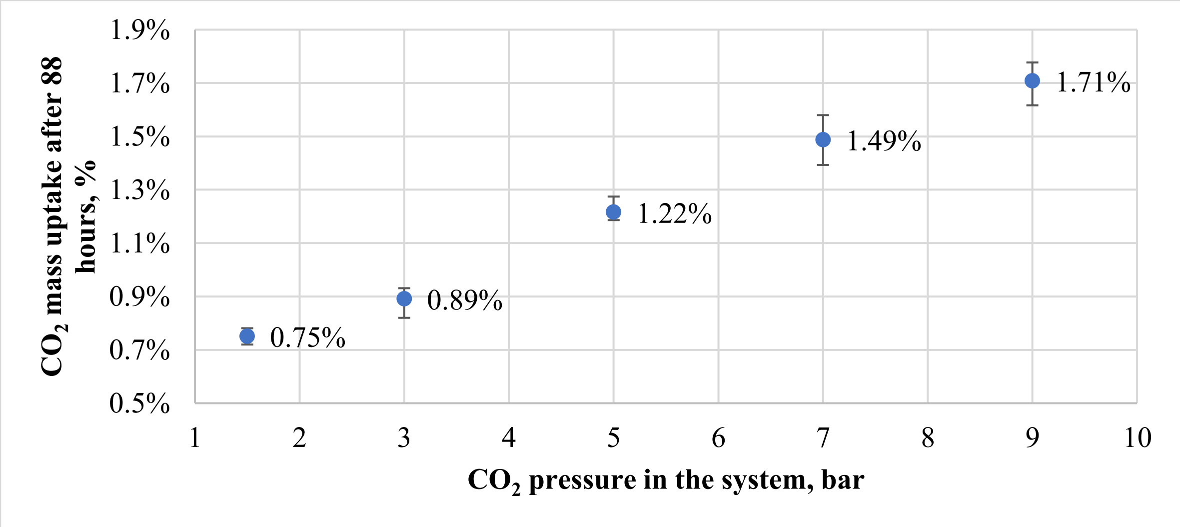


Figure 4.15: CO_2 mass uptake after 88 hours of exposure to a CO_2 atmosphere at different pressures and at room temperature for modified bitumen.

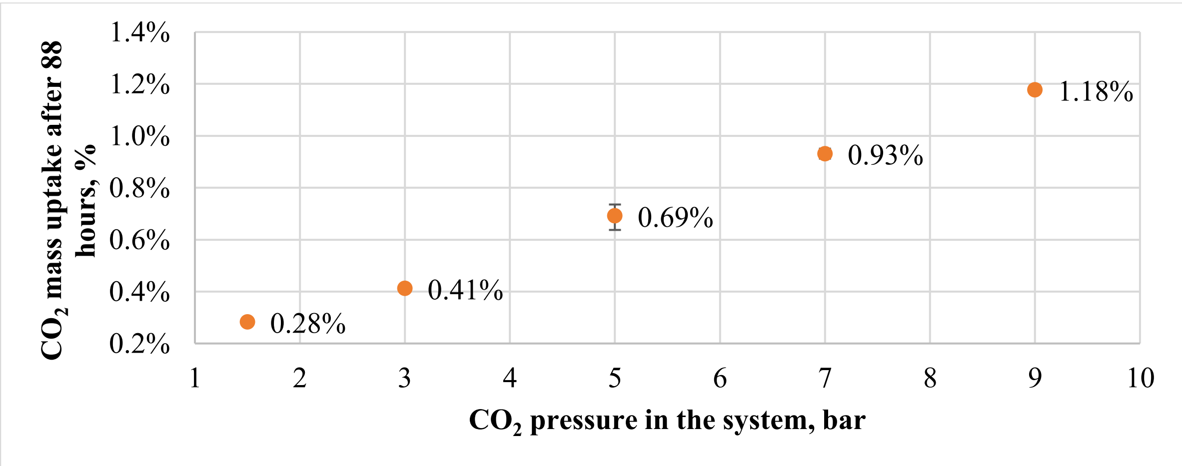


Figure 4.16: CO_2 mass uptake after 88 hours of exposure to a CO_2 atmosphere at different pressures and at room temperature for classic bitumen.

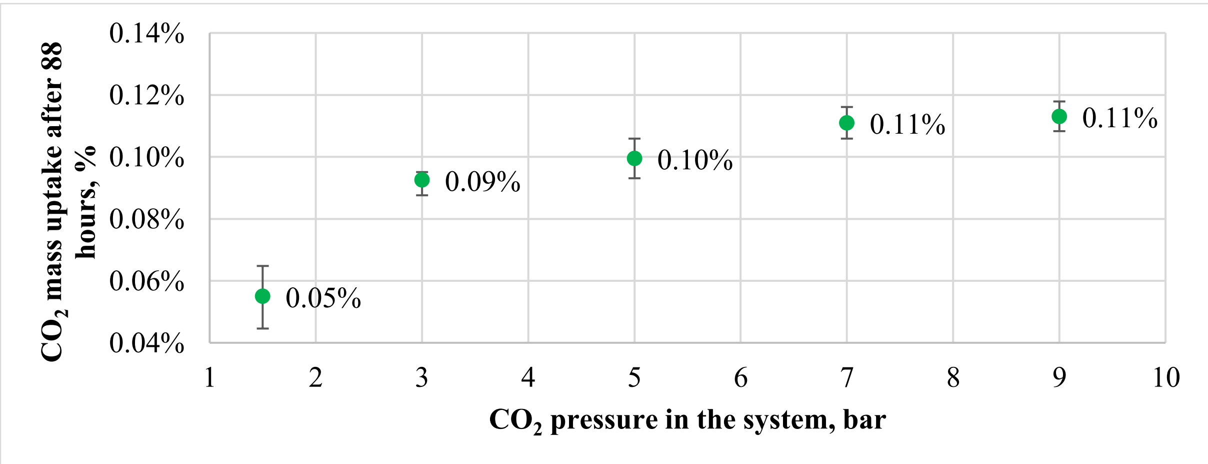


Figure 4.17: CO_2 mass uptake after 88 hours of exposure to a CO_2 atmosphere at different pressures and at room temperature for RAP.

Experimental points obtained at room pressure and discussed in the previous chapter have not been included in the graphs because the experimental approach and the experimental setup are different in the former case the pressure is constant and there is a constant flow of CO_2, in the latter the vessel is closed, and the pressure decreases until the thermodynamic equilibrium is reached.

As can be seen in Figures 4.15 and 4.16, the experimental points associated with CO_2 mass uptake after 88 hours of exposure, for both modified bitumen and unmodified bitumen, follow a linear pattern. In the case of asphalt aggregates the uptake value after 88 hours seems to stabilize around 0.1% already at 3 bars of pressure.

Although there are no appreciable results in the literature for this experimental range of pressures, it is possible to analyze the results in relation to those presented in the first chapter, in particular to Mehrotra and Svrcek ones [35]. Although those are thermodynamic equilibrium values, that is, maximum capacity, and the results just presented are not, it can be noted that for relatively low pressures the curve is also linear. In addition, the order of magnitude of the maximum solubility expressed as a percentage mass is the same as that of these results.

Another comparison, more relevant, can be made with the results shown in the figure 2.12, which shows the CO_2 solubilization curve in two bitumen samples subjected to a pressure of 40 psi (2.75 bar) at room temperature. In that work the bitumen uptake after more than 170 hours is between 0.3% and 0.4%, according to the bitumen formulation. Moreover, their model allows to estimate a CO_2 mass uptake after 88 hours between 0.22% and 0.27%, depending on the bitumen grades. These values are lower than the one found in this work (about 0.41%) but it is consistent, especially considering that the bitumen formulations present different physical and chemical characteristics and composition, and that a higher pressure has been applied in this work (3 bars instead of 2.76 bars).

Both curves associated to the two types of bitumen grow linearly more or less with the same speed: by interpolating data with a linear model, the linear coefficient obtained is about the same. Instead, the curve relative to the asphalt Aggregates grows more and more slowly, stabilizing itself around a value of 0.11%. These materials consist only of a small percentage of bitumen. At 3 bar the aggregate asphalt mass uptake turns out to be just less than a quarter of the unmodified bitumen uptake at the same pressure conditions (0.09% vs 0.41%).

4.2.2. Characterization of the solubilization kinetics

The kinetics of the solubilization process under $P > P_{amb}$ conditions have been defined by monitoring the sample mass over time, measuring the uptake change in mass over 160 hours. This characterization has been made for the case at 3 bars and at 9 bars. The related results are showed in figure 4.18 and 4.19.

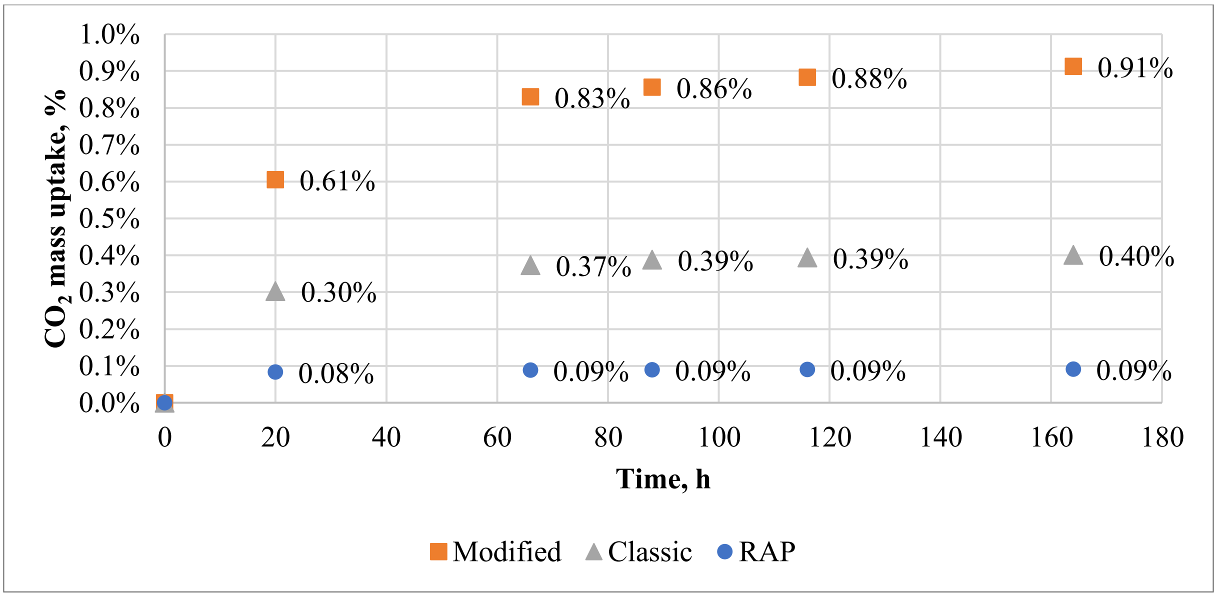


Figure 4.18: Evolution over time of the CO_2 mass uptake for both bitumen formulations and asphalt aggregate, when exposed to a CO_2 atmosphere at 3 bars.

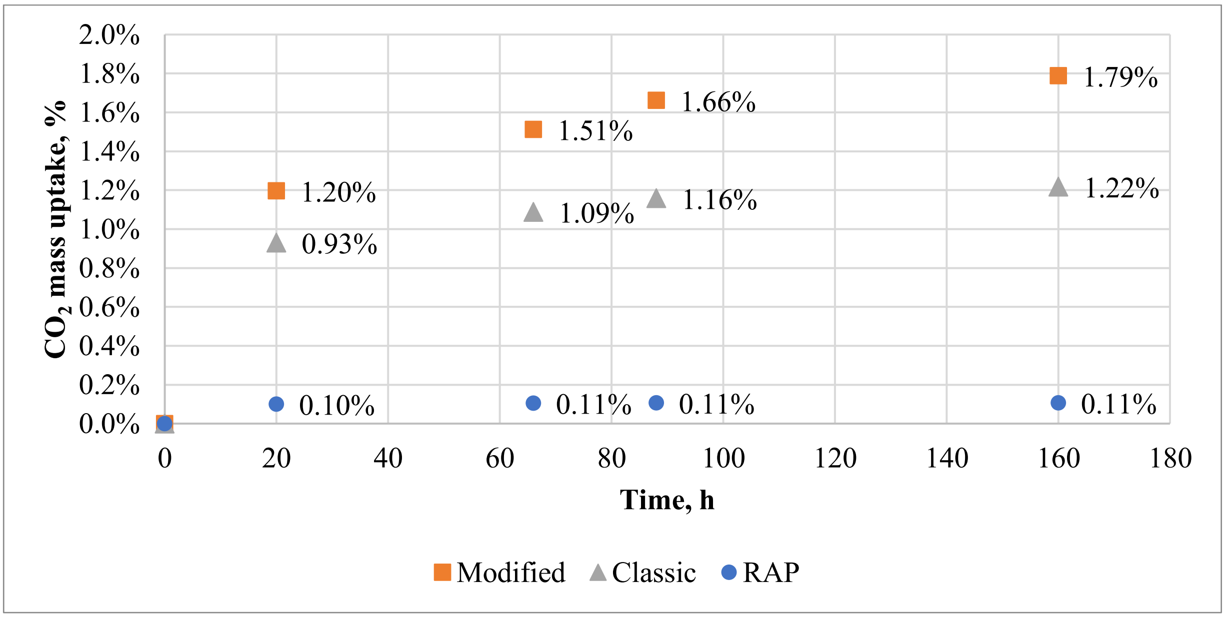


Figure 4.19: Evolution over time of the CO_2 mass uptake for both bitumen formulations and asphalt aggregate, when exposed to a CO_2 atmosphere at 9 bars.

In this second step it has been more complex to construct models for the evaluation of the solubilization kinetics. In fact, to characterize the evolution of the samples mass it is necessary to progressively weigh the samples, and since the weighing system was not integrated in the vessel, it is necessary each time to depressurize the system, open the vessel, carry out the measurements, reseal the vessel and pressurize the system again. For this reason, in the 9 bars experience less experimental points have been collected compared to the 3 bars experience.

Unlike the room pressure case, for which the measurement process took a few tens of seconds, in this case it takes a few minutes. This means that during the mass measurement procedure, a not negligible desorption phenomenon may occur, especially in the case of Asphalt

Aggregates, for which, as will be illustrated below, desorption kinetics are very fast in the first few minutes.

In fact, by measuring the mass of the samples progressively, they are likely to lose a certain amount of CO_2, and when they are put again in the vessel, the phenomenon of solubilization starts again but from an uptake value lower than what it would have been if no measure had been taken.

To verify the extent of this phenomenon and to evaluate the quality of the results obtained by this technique, the 88 hours uptake values obtained without making any intermediate measure, (through an uninterrupted solubilization process), are compared with the uptake values obtained carrying out two mass measurements first (at 20 hours and 66 hours), by depressurizing the vessel, exposing the samples to free air, and re-establishing the pressure, two times. The comparison is showed in table 4.5.

Table 4.5: Comparison between the CO_2 mass uptakes after 88 hours of CO_2 exposition for the case without intermediate measures and for the case with intermediate measures.

Pressure, bar	**Type of sample**	**CO_2 mass uptake after 88 hours, %**		
		Without intermediate measures		With intermediate measures
		Average value	Experimental range	
3	Modified bitumen	0.891%	0.819% - 0.931%	0.856%
	Classic bitumen	0.412%	0.410% - 0.413%	0.398%
	Asphalt aggregates	0.093%	0.088% - 0.095%	0.090%
9	Modified bitumen	1.709%	1.617% - 1.777%	1.662%
	Classic bitumen	1.177%	1.168% - 1.193%	1.159%
	Asphalt aggregates	0.113%	0.108% - 0.118%	0.107%

As can be seen from the table, the uptake values obtained by carrying out intermediate weighing are always lower than the corresponding average values obtained with the uninterrupted process (without intermediate weighing). This detail confirms the presence of a non-negligible desorption phenomenon that occurs during the sample mass measurement process, which is further confirmed because in some cases the values are also slightly below the experimental range lower value.

Nevertheless, many of the values obtained fall within the experimental range, indicating that the desorption phenomenon, although present, is relatively limited and has an effect on the results comparable to that of the experimental error defined by the realization of multiple measurements with multiple samples. This means that this procedure influences the experimental data variability of the same order of magnitude of the experimental error, confirming the validity of its results.

As in the case of data obtained from experiments at room pressure, we have used the experimental data to construct a model that allows the prediction of the CO_2 maximum solubilization capacity in the investigated materials, and that allows to characterize the process kinetics. The Peleg model is selected once more, which has been already used in the previous chapter to characterize the kinetics of the process under room pressure conditions. As in the previous case, several possible linearisations have been carried out, then choosing the couple of parameters that maximize the coefficient of determination and therefore that provide the model with the highest quality.

The model results and the relative parameters are resumed in table 4.6.

Table 4.6: Peleg model parameters for the solubilization process at 3 and 9 bars

Pressure, bar	Type of sample	k, h^{-1}	x_e	RSQ
3	Modified	8.299	0.98%	99.995%
	Classic	31.086	0.42%	99.990%
	Asphalt aggregates	502.728	0.092%	99.994%
9	Modified	4.379	1.88%	99.611%
	Classic	10.905	1.25%	99.790%
	Asphalt aggregates	545.949	0.11%	99.997%

The first element that can discussed is the maximum solubilization capacity that is represented by the model parameter x_e. In the modified bitumen case, for both pressures, this value is appreciably higher than the 88-hour experimental value: 0.98% vs 0.89% at 3 bars and 1.88% vs 1.71%. This indicates that this bitumen formulation does not reach maximum uptake values within the first 100 process hours.

This is also demonstrated by the parameter k, which represents the rate at which the curve grows. For both pressures (and in the ambient pressure case) this value in the order of units, relatively small compared to the corresponding values associated with the other bitumen formulation and asphalt aggregates. Ultimately, although this bitumen formulation has a higher maximum capacity than the unmodified bitumen, presents a slower solubilization kinetics, meaning that it takes longer to reach its maximum capacity. Graphically this is appreciable by the fact that the curve associated with this material grows less quickly than the curves for the other samples.

In the classic bitumen case, the maximum capacity value is also higher than the experimental 88-hours measured value. However, it is possible to observe a difference in the characteristics of the two curves: the kinetic constant associated with the 3 bars process is about 3 times greater than the kinetic constant associated with the 9 bars process. (And in turn the kinetic constant of the room pressure process is about 3 times larger than the 3 bars one).

This means that, despite the uptake of CO_2 increases linearly as pressure increases, the kinetics of the process decreases progressively, that is, the solubilization curve grows more slowly. If at ambient pressure the value reached in the first 88 hours is close to the maximum capacity, in the case of 9 bar instead there is still a considerable gap between the uptake achieved and the maximum possible capacity.

Finally, the CO_2 adsorption process by asphalt Aggregates is the one with the highest kinetics since the parameter k is in both cases of the order of several hundreds.

In figures 4.20 and 4.21 the model curves are showed in comparison with the respective experimental data.

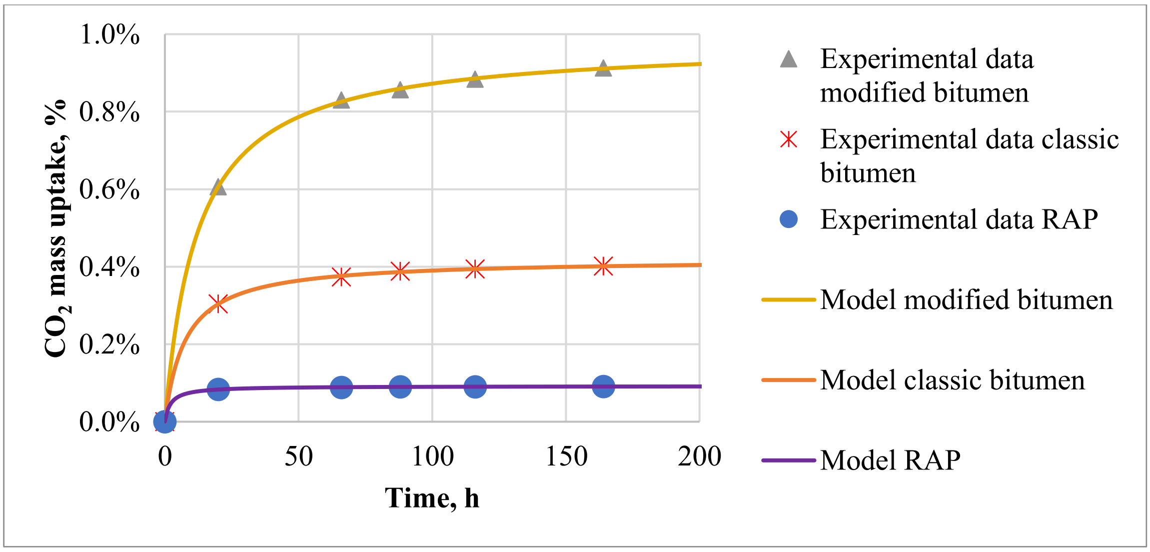


Figure 4.20: Comparison between the Peleg model curves and the experimental points for the solubilization process for the two bitumen formulations and the asphalt aggregates at 3 bars.

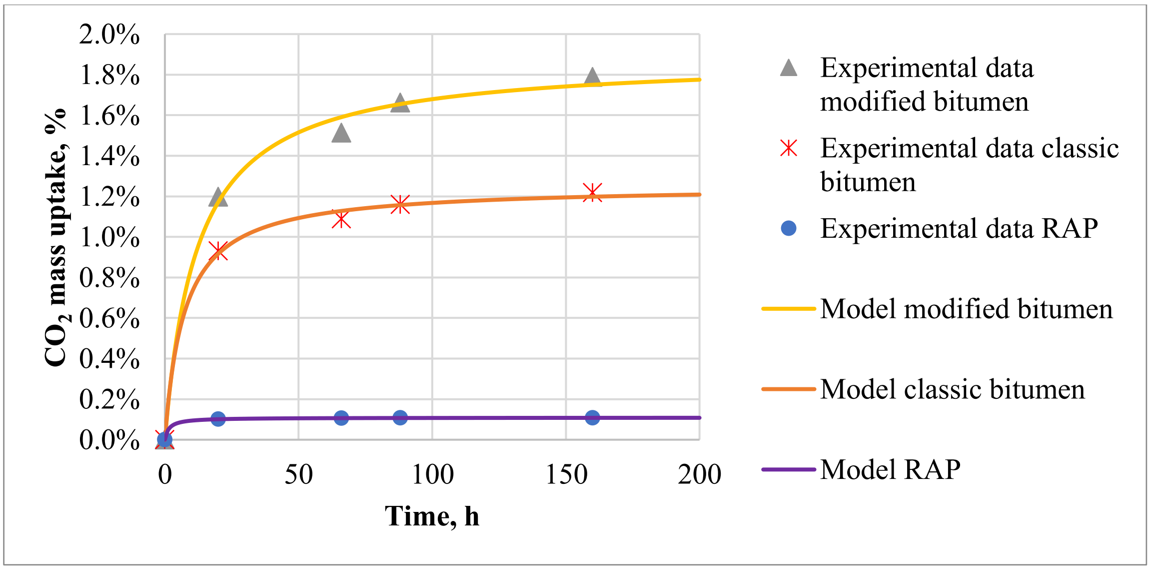


Figure 4.21: Comparison between the Peleg model curves and the experimental points for the solubilization process for the two bitumen formulations and the asphalt aggregates at 9 bars.

4.2.3. 20 bars results

As the last phase of this higher-pressure solubilization capacity characterization, the samples are exposed to a 20 bar CO_2 atmosphere for 88 hours, so that these experimental results could be compared with the results of the same experiments conducted at lower pressures (0-9 bar).

The results of this experience are shown in figure 4.22, where they are compared with the results for all the other investigated pressures for all the studied materials. The pressure is expressed in bar, where 0 bar indicates atmospheric pressure, that is the experimental conditions of the first step of this work.

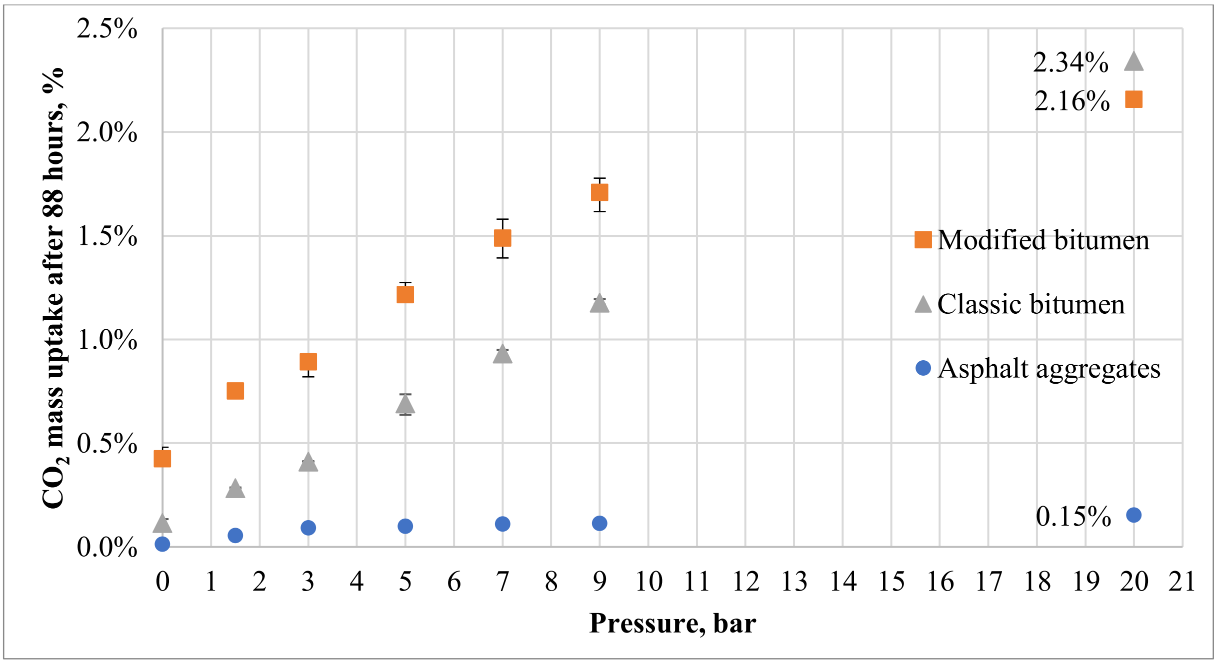


Figure 4.22: CO_2 uptake after 88 hours of CO_2 exposition, results for 20 bars compared with lower pressures results.

As can be seen from the figure, the results of the 20 bars experiment confirm the linear scheme followed by classical bitumen, since after 88 hours of exposure to 20 bar the sample solubilizes a quantity of carbon dioxide equal to 2.34% of its mass.

The result for RAP also confirms that the material seems to have reached an upper limit due to the saturation of adsorption sites, as the uptake value at 20 bar is 0.15%, a little further from 0.11% obtained at 9 bars.

The result associated with modified bitumen, on the other hand, does not follow the linear trend suggested by the results of previous experiments, and for the first time during the entire experimental work, classic bitumen sample appears to have solubilized more CO_2 than modified bitumen 2.16% for modified bitumen vs 2.34% for classic bitumen.

However, this result cannot be used to hypothesize a hypothetical CO_2 saturation phenomenon of modified bitumen in contrast to the behavior of classic bitumen, this is because the method chosen for the characterization, once again the gravimetric method, has some limits that have increasingly important consequences on the quality of the results as the experience pressure increases.

If during the solubilization process higher pressures are used, the samples solubilize more carbon dioxide, then, when the reactor is depressurized, as it is explained in paragraph 4.2.5, the desorption process is the faster the higher the amount of solubilized CO_2, and this is particularly true for the modified bitumen. Furthermore, the use of a very high pressure considerably lengthens the depressurization process, increasing by several minutes the time between the end of the solubilization process and the experimental measurement.

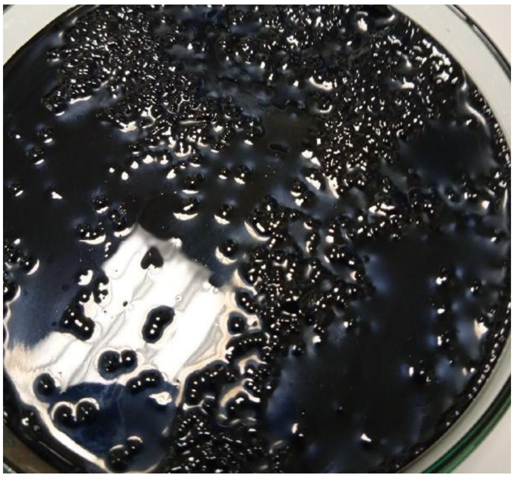
This means that the measured value is an understatement of the real value, since during the process of depressurization, reactor opening and mass measurement, a not negligible and not quantifiable amount of CO_2 was lost, and apparently, at 20 bar, this phenomenon can be no longer ignored, making this experimental method not suitable for such high pressures and such materials.

4.2.4. Changes in bitumen texture

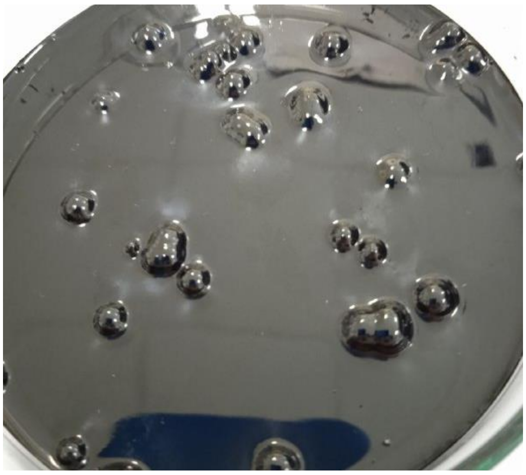
An interesting phenomenon that clearly shows that the increase in pressure leads to the solubilization of amounts of CO_2 that would not be possible to solubilize at ambient pressure, was observed during this phase of the work. This phenomenon was observed in the air exposure phase, described in paragraph 4.2.5.

After the samples are taken from the reactor and exposed to free air, within a few minutes the progressive formation of bubbles in bitumen can be appreciated. This happen because the moment the cell is depressurized, the CO_2 inside the bitumen desorbs and expands, forming such bubbles and modifying the texture of the material. The higher the pressure to which the sample has been subjected during the solubilization phase, the higher the amount of dissolved CO_2, the larger the bubbles number and size. If the sample is subjected to higher pressures, the bubbles form and expand faster, as the amount of CO_2 that is desorbed is higher and the desorption process is faster.

In Figure 4.23 it is possible to see samples of both formulations subjected to 5 and 9 bars, in which the formation of bubbles was observed during free air exposure.



a. Modified bitumen exposed to a 5 bars atmosphere



b. Classic bitumen exposed to a 5 bars atmosphere

c. Modified bitumen exposed to a 9 bars atmosphere

d. Classic bitumen exposed to a 9 bars atmosphere

Figure 4.23: Texture of the two bitumen formulations after CO_2 exposure.

4.2.5. Characterization of the CO_2 release kinetics

As in the first phase of the experimental analysis, after the end of the characterization of each solubilization process, the samples were placed in contact with the atmosphere under ambient conditions, to characterize the CO_2 release kinetics. All samples exposed to free air have been progressively weighed. All of them have progressively lost mass, due to the desorption of the CO_2 contained in the samples.

It was then possible to build CO_2 uptake vs time curves, in which it is possible to see how the amount of CO_2 solubilized or adsorbed by the samples decreases progressively, starting from the maximum value corresponding to the moment the samples are taken from the pressurized cell up to a minimum equilibrium value.

The main purpose of this experimental phase was to characterize the minimum equilibrium value, namely the CO_2 naturally retained in the sample (the definition of which is important to judge whether these materials can be considered as good candidates for CO_2 storage) and the kinetics of the process, that is, how fast this desorption takes place.

Figures 4.24 and 4.25 show the CO_2 mass uptake evolution over time, starting from the moment the samples are taken out from the vessel and exposed to free air, for the samples previously exposed to a 3 bars atmosphere, for modified bitumen and classic bitumen respectively. The results related to the other pressure conditions (1.5 bars, 5 bars, 7 bars, 9 bars) are available as annexes.

The modified bitumen samples that have been exposed to a 3 bars atmosphere (figure 4.24) start from an uptake value of 0.81%-0.93% and, when exposed to free air they progressively release CO_2, loosing mass, until after more than 160 hours they stabilize around 0.52%. The classic bitumen samples exposed to the 3 bars atmosphere (figure 4.25) start around 0.42% and after more than 160 hours they reach an equilibrium value between 0.052% and 0.058%.

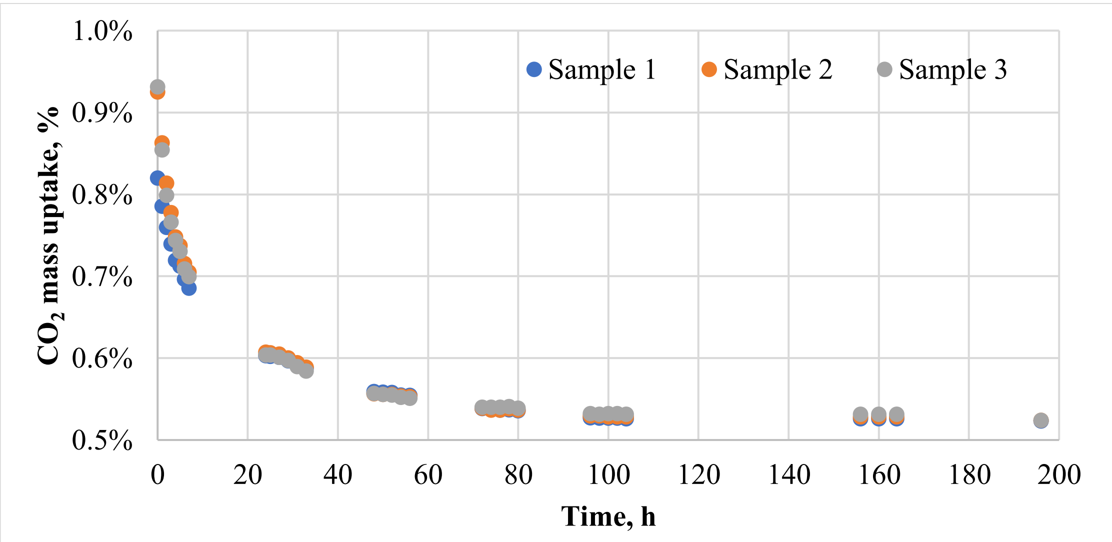


Figure 4.24: CO_2 mass uptake evolution over time for modified bitumen samples exposed to free air that have been originally exposed to a CO_2 atmosphere at 3 bars.

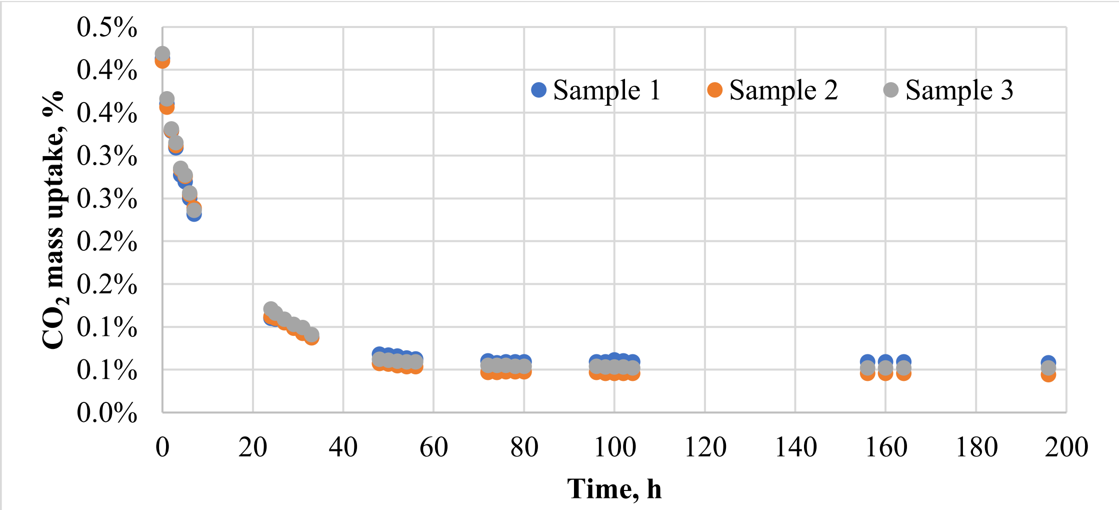
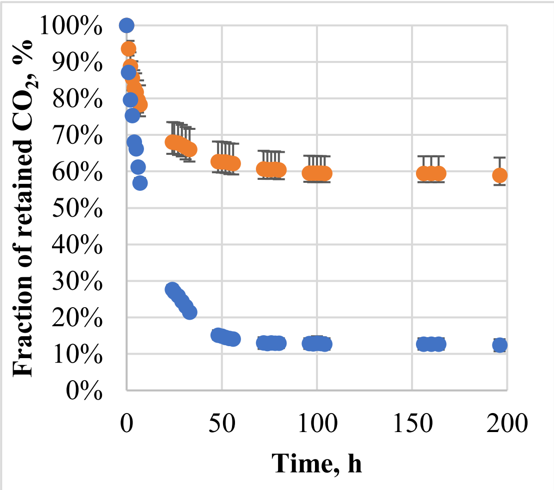
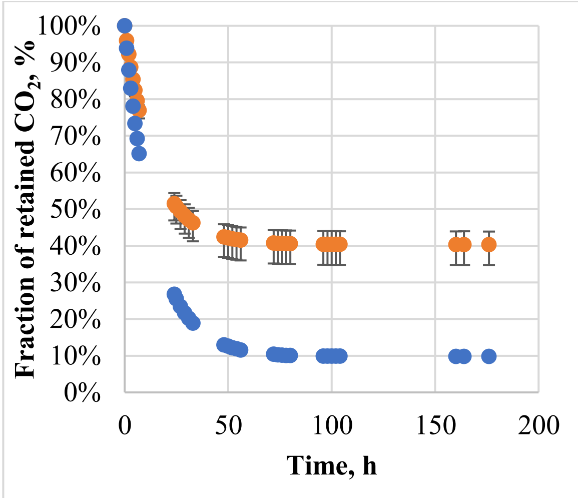


Figure 4.25: CO_2 mass uptake evolution over time for classic bitumen samples exposed to free air that have been originally exposed to a CO_2 atmosphere at 3 bars.

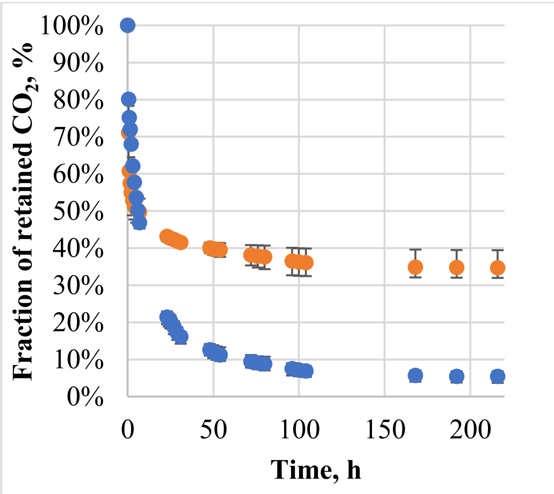
In addition to expressing the amount of CO_2 retained in the sample as mass fraction, which is the ratio to the original sample mass before exposure to the atmosphere of pressurized CO_2, the CO_2 quantity can be also expressed as the fraction of the CO_2 amount that the sample contains at the beginning of the release process (as soon as it is taken from the pressurized cell). This type of graph, of which some examples can be seen in figure 4.26, starts at 100% and ends at a final equilibrium value that corresponds to the fraction of the amount initially absorbed/adsorbed by the sample, that the material can retain after at least 160 hours of exposure to free air.



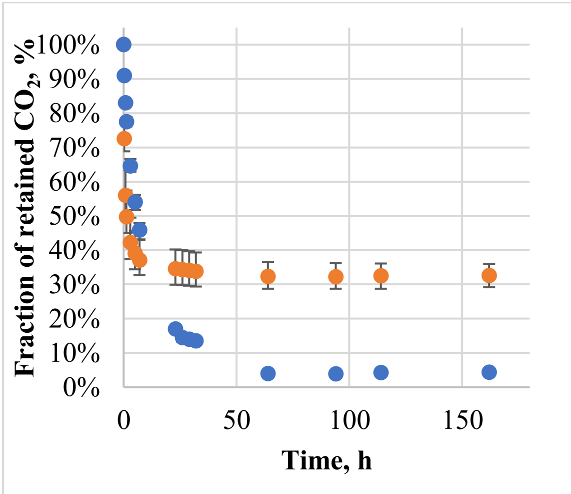
a. Samples previously exposed to a **3 bars** CO_2 atmosphere



b. Samples previously exposed to a **5 bars** CO_2 atmosphere



c. Samples previously exposed to a **7 bars** CO_2 atmosphere



d. Samples previously exposed to a **9 bars** CO_2 atmosphere

Figure 4.26: Fraction of the originally solubilized CO_2 that is retained by the two bitumen formulations when exposed to free air conditions; • modified bitumen; • classic bitumen

The results for the two types of bitumen are summarized in Table 4.7, where they are classified according to the pressure to which the samples have been subjected in the solubilization process. In the third column of the table it is possible to read the average mass uptake (%) reached by the samples after 88 hours of exposure to CO_2 in the pressurized vessel, in the fourth column the mass uptake after at least 160 hours of free air exposition and in the fifth column the average retained CO_2 (expressed ad percentage of the initial maximum value), which corresponds to the mass uptake at the end divided by the mass uptake at the beginning of the desorption experience.

Table 4.7: Results for the CO_2 release process of samples previously exposed to CO_2 pressures higher than atmospheric pressure.

Type of sample	Pressure of the solubilization process, bar	Average CO_2 uptake at the end of the solubilization process, %	Average CO_2 uptake after at least 160 hours of free air exposition, %	Average retained CO_2, %
Modified bitumen	0 (ambient pressure)	0.43%	0.35%	80.9%
	1.5	0.75%	0.46%	60.1%
	3	0.89%	0.52%	58.9%
	5	1.22%	0.49%	40.3%
	7	1.49%	0.52%	34.6%
	9	1.71%	0.56%	32.5%
	20	2.16%	0.48%	22.2%
Classic bitumen	0 (ambient pressure)	0.11%	0.04%	32.2%
	1.5	0.28%	0.01%	4.2%
	3	0.41%	0.05%	12.4%
	5	0.69%	0.07%	9.9%
	7	0.93%	0.05%	5.4%
	9	1.18%	0.06%	4.3%
	20	2.34%	0.08%	3.4%

As regards modified bitumen it can be noticed that even if the initial CO_2 mass uptake value increases as the pressure increases, the final value after at least 160 hours of free air exposure is always around 0.5%. This means that the retained value expressed as percentage of the initial value decreases with increasing pressure, not because it decreases in absolute value, but because it decreases in relation to the amount that we were able to solubilize.

The Classic bitumen results follow the same principle: the increase in pressure increases the maximum amount that can be solubilized after 88 hours, but after at least 160 hours of exposure to free air the retained amount is between 0.05% and 0.07%, a much smaller quantity than modified bitumen. Also in this case, the retained value expressed as percentage of the initial value decreases with increasing pressure (except for the 1.5 bars value) because it decreases in relation to the amount that we were able to solubilize.

Figures 4.27 and 4.28 show the average retained CO_2 after the release process, expressed as percentage of the starting value, as a function of the CO_2 pressure of the solubilization phase. In these graphs there are also the values corresponding to the desorption process carried out on the samples of the first experimental phase conducted at ambient pressure (0 bar indicates the atmospheric pressure conditions).

The monotonous decreasing trend is confirmed, but it is necessary to underline that the experimental points at 1.5 bar seem not to follow the curve trend. In both cases the samples desorbed more than one would expect by observing this trend, in the case of classic bitumen, the sample retained only 0.01% in terms of CO_2 mass uptake, this inconsistency is probably linked to the lack of temperature control during the experimental process: a local rise in temperature may have accelerated the desorption process and led the samples to retain smaller CO_2 amounts.

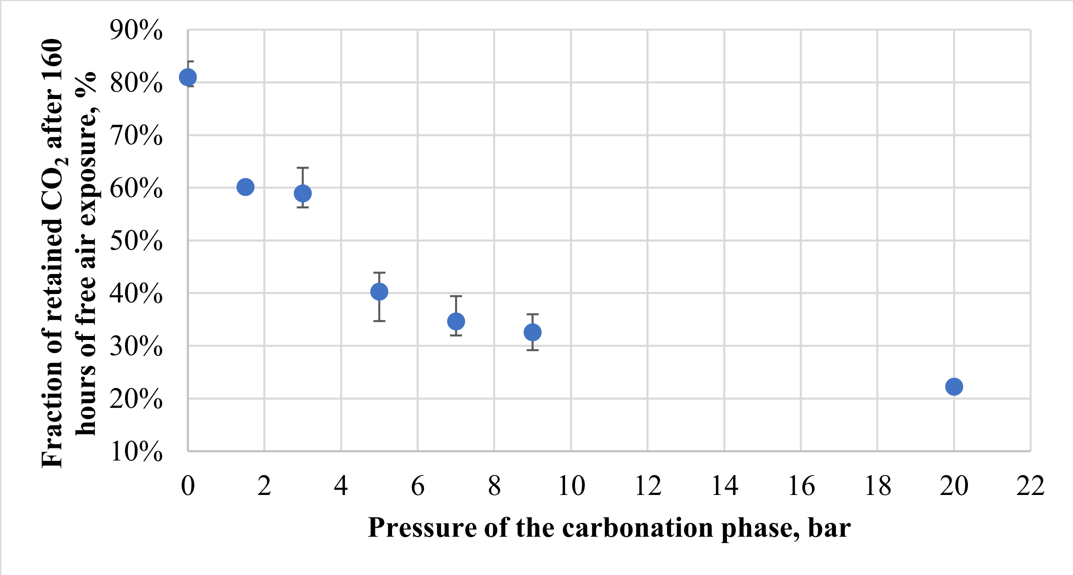


Figure 4.27: Average retained CO_2 after the release process, expressed as percentage of the starting value, as a function of the CO_2 pressure of the solubilization phase for modified bitumen.

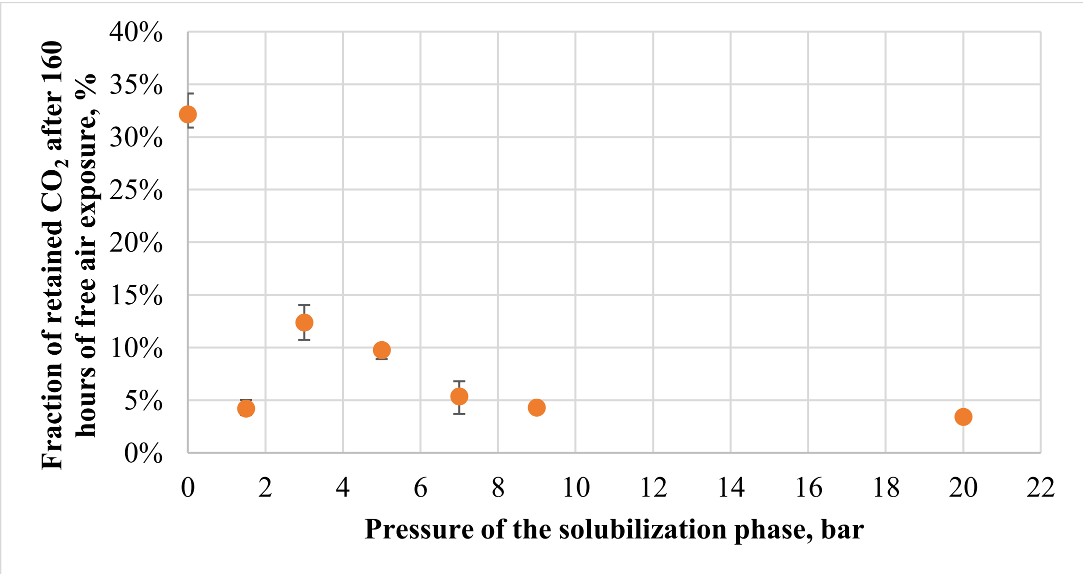
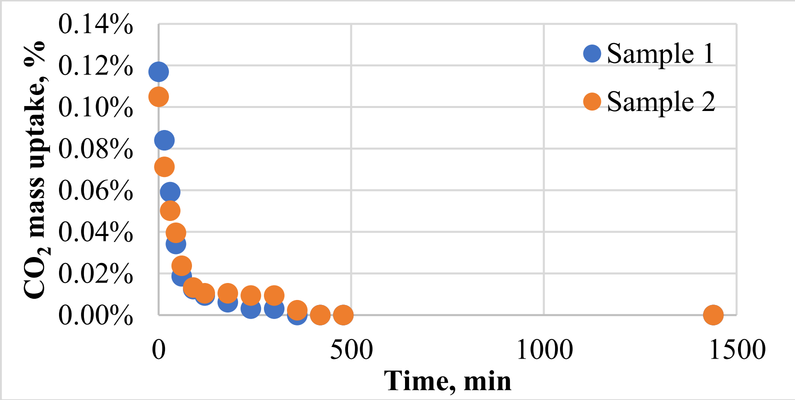
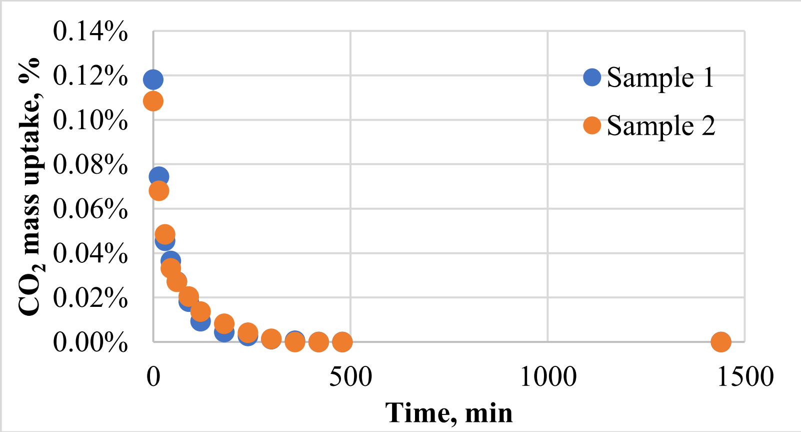


Figure 4.28: Average retained CO_2 after the release process, expressed as percentage of the starting value, as a function of the CO_2 pressure of the solubilization phase for classic bitumen.

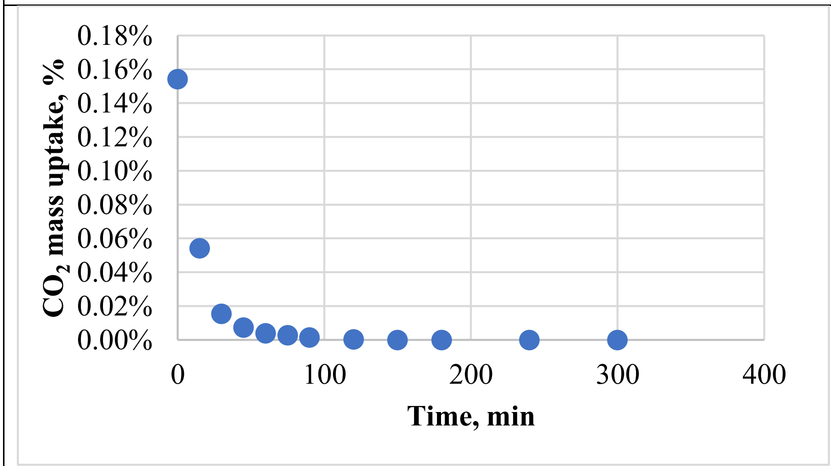
As for the CO_2 release process of RAP samples, the evolution of CO_2 mass uptake after these samples were exposed to free air has been characterized. Figure 4.29 shows the CO_2 mass fraction as a function of time for the samples that were originally exposed to 7, 9 and 20 bars CO_2 atmosphere. The CO_2 release process of such samples is the one with the highest kinetics, as in few hours the samples lose up to 90% of the original content. After a maximum of 4 hours the samples have completely lost the previously adsorbed CO_2.



a. RAP samples previously exposed to a **7 bars** CO_2 atmosphere



b. RAP samples previously exposed to a **9 bars** CO_2 atmosphere



c. RAP samples previously exposed to a **20 bars** CO_2 atmosphere

Figure 4.29: CO_2 mass uptake as a function of time in the CO_2 release phase for the asphalt aggregates.

4.3. *Step 3: Gas Phase Chromatography results*

The chromatogram of the Alkane standard solution C_8-C_{20} is presented on figure 4.30. One can identify the compounds and then the time for each alkane.

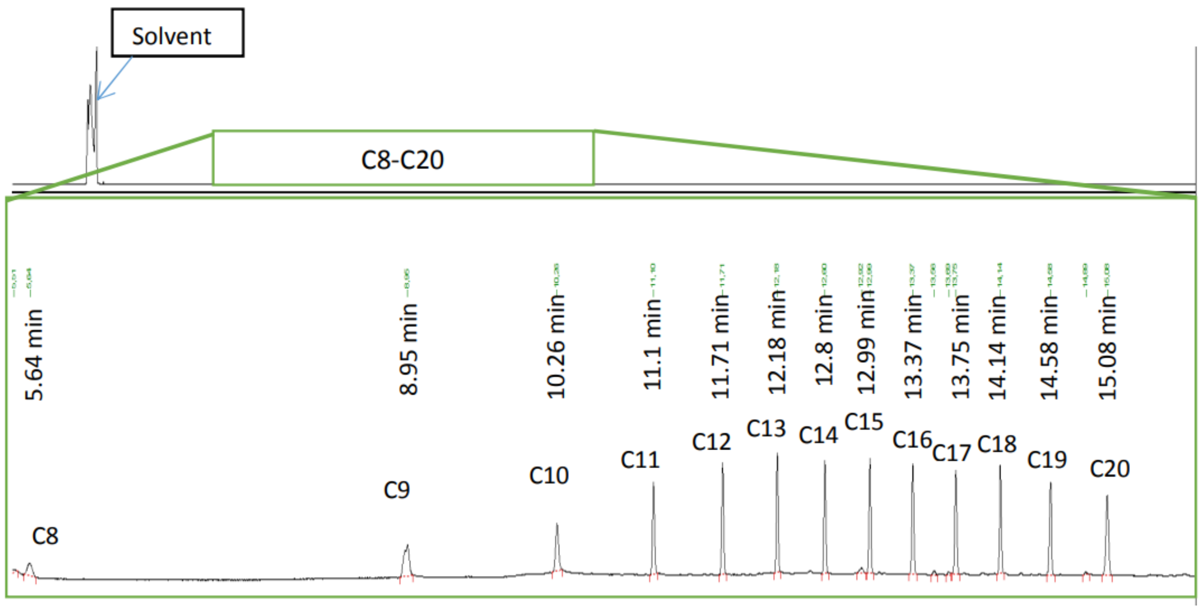


Figure 4.30: Chromatogram for the C_8-C_{20} mix with selected temperature program.

The total number of peaks for each temperature for both bitumen formulations is reported in table 4.8.

For both bitumen formulations' fumes, the total number of peaks detected increases with increasing temperature. In the modified bitumen case, at 80 °C, 38 distinct peaks are detected, and at 160 °C the GPC detects up to 80 peaks. In the classic bitumen case, the GPC returns a chromatogram with 39 peaks at 80°C, and one with 76 peaks at 160°C.

Clearly, an increase in temperature leads to the release of more volatile components from the bitumen samples, and the gaseous phase that constitutes the fumes present in the reactor head is then enriched in terms of components.

It was not possible to observe substantial differences in peak numbers between the two bitumen formulations, generally the number found is very similar at the same temperature, in some cases this number is slightly higher for modified bitumen and in other cases for classic bitumen, but there is no trend that shows how one of the two formulations releases a higher number of volatile components than the other.

Regarding the alkane presence, it was observed more peaks corresponding to alkane C_8-C_{20} on the classic sample than for the modified sample. The treatment at which the modified sample has been subjected can be the reason of the decrease of the alkane peaks.

Table 4.8: Number of peaks and identified alkanes following the fumes' GC analysis, in red the alkanes for which stronger peaks have been observed.

Temperature, °C	Modified bitumen		Classic bitumen	
	Identified alkanes	N° of peaks	Identified alkanes	N° of peaks
80	**C_{10}**, C_8, C_{11}, C_{14}, C_{18}	38	**C_{10}**, C_8, C_9, C_{11}, C_{12}, C_{14}, C_{18}	39
100	**C_{10}**, **C_{11}**, C_8, C_9, C_{13}, C_{18}	57	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{14}, C_{18}	53
120	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	62	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	59
140	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	63	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{18}	67
160	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{17}, C_{18}	80	**C_9**, **C_{10}**, **C_{11}**, **C_{12}**, C_8, C_{13}, C_{14}, C_{15}, C_{17}, C_{18}	76

5. Conclusions

5.1. Results summary

The results obtained from the experiments carried out in this work have made it possible to characterize the CO_2 solubilization/adsorption process in bituminous materials under ambient conditions, for which it was not possible to find useful information in scientific literature. The CO_2 solubilization in bituminous materials is in fact the subject of several studies but carried out at relatively high pressures since the main practical application of this process (CO_2-EoR) requires pressures of several tens of bars.

In the first part of the work, the CO_2-bitumen and CO_2-RAP systems are investigated under ambient temperature and pressure, modified bitumen presents CO_2 uptake values between 0.39% and 0.47%, about four times that of classic bitumen, which uptake varies between 0.09% and 0.13%. The asphalt aggregates can adsorb slightly more CO_2 than 0.01% of its mass, an amount so small that it excludes any hypothesis of practical application of this process.

The kinetics of the solubilization process were characterized by recording the masses several times during the duration of the whole experiment and plotting the CO_2 mass uptake as a function of time. With these data it has been possible to model the CO_2 solubilization/diffusion kinetics. According to this model, the maximum value for the CO_2 uptake in modified bitumen would be on average 0.53%, while for classic bitumen, the model foresees an average maximum capacity of 0.12%. The kinetics of classic bitumen solubilization process is faster, as the sample reaches values close to the maximum capacity in a much smaller time than that of the modified bitumen.

The CO_2 release process has been characterized: for modified bitumen after 9 days of desorption the sample is able to retain between 0.32% and 0.39% of CO_2 (81% of the maximal value at the start of the desorption process) which is more than five times the average CO_2 mass concentration in air (0.063%). Classic bitumen loses most of the absorbed CO_2: after 9 days, this formulation holds on average only 32% of the starting amount, which is less than 0.04% expressed in CO_2 mass uptake.

In the second part of the work, experimental pressures up to 10 bar were utilized. CO_2 mass uptake after 88 hours of exposition increases linearly with increasing pressure. The curve relative to the asphalt Aggregates seems to present a maximal CO_2 mass uptake value of 0.11%.

Peleg equation was once more used to model the process kinetics at 3 and 9 bars. According to this model the modified bitumen presents a maximum solubilization capacity of 0.98% at 3 bars and 1.88% at 9 bars, and a kinetic parameter k in the order of units. Modified bitumen formulation has a higher maximum capacity than the unmodified bitumen (which is 0.42% at 3 bars and 1.25% at 9 bars), but it presents a slower solubilization kinetics, meaning that it takes longer to reach its maximum capacity.

The samples exposed to $P>P_{amb}$ have then been exposed to free air conditions to characterize the CO_2 release process. For modified bitumen, even if the absorbed CO_2 amount increases as the pressure increases, the final value after at least 160 hours of free air exposure is always around 0.5%. The classic bitumen results follow the same principle: the increase in pressure increases the maximum amount that can be solubilized after 88 hours, but after at least 160 hours of exposure to free air the retained amount is between 0.05% and 0.07%, a much smaller quantity than modified bitumen. As for the RAP samples, in few hours they lose up to 90% of the original content. After a maximum of 20 hours the samples have completely lost the adsorbed CO_2.

The Gas Phase Chromatography analysis has allowed to partially characterize the volatile compounds that constitute the fumes generated when both bitumen formulations are heated up to 160 °C. It has been clearly observed that an increase in temperature leads to the identification of a higher number of peaks in the chromatograms, and thus a higher number of released components. However, no appreciable differences could be observed between the two bitumen formulations fumes CG. The chromatograms have in both cases peaks associated with the alkanes C_9-C_{10}, and less clearly with the alkanes C_{13}-C_{18}.

5.2. Results discussion and possible applications

The most interesting results concern modified bitumen. Thanks to this work, it has been possible to verify that in this bitumen formulation it is indeed possible to solubilize a much greater amount of CO_2 than in classical bitumen. The maximum retention capacity of modified bitumen is four times higher than unmodified bitumen. If samples are treated at $P>P_{amb}$ the difference between the retention capacities is reduced, but in any case, modified bitumen remains, among the materials analyzed, the one that can solubilize the greater amount of CO_2.

The practical interest of this process applied to modified bitumen is identifiable in the fact that this material can retain a non-negligible CO_2 amount, even after more than 9 days. (0.5% on average; the mass fraction naturally present in the air being around 0.063%).

The kinetics of the solubilization process, both in ambient pressure and in $P>P_{amb}$ experiments, is slower in the case of modified bitumen and faster in the case of classic bitumen. For modified bitumen it is necessary to wait more than a week to reach values close to the maximum capacities defined in our work. Moreover, the pressure at which the process takes place does not seem to have any effect on the kinetics of the process (In the kinetic models realized, the kinetic constant is always of the order of the units).

As for classic bitumen, kinetics is much faster, allowing to reach values close to the maximum capacity in less time (4-5 days), which is particularly true in the case of the process at atmospheric pressure or at low pressures. As the pressure increases, it is true that classical bitumen increases its maximum solubilization capacity, but it is also true that the kinetics of the process slows down. (The kinetic constant is about 90 at ambient pressure, about 30 at P=3 bars and about 10 at P=9 bars). This means that although it is possible to solubilize larger CO_2 amounts in classic bitumen by increasing the pressure, it is necessary to spend more time.

The Asphalt Aggregates, on the other hand, have a very low adsorption capacity if exposure occurs at ambient P (around 0.01%), but if exposure occurs at $P>P_{amb}$, this material can adsorb up to 0.1% in mass. Although it is not a negligible quantity, it loses its practical applicability when it is observed that the desorption process (as well as that of adsorption) is incredibly fast, and samples lose the entire amount of CO_2 adsorbed within a few hours.

5.3. Perspectives

Although the presented work has allowed to obtain many interesting results and to characterize a phenomenon little investigated in the scientific literature under these experimental conditions, the results obtained require further investigation, laying the basis for further work in continuity with the data presented in this report. These results open the way to different possibilities and perspectives, with the aim of completing the non-exhaustive investigations carried out in this work, and to try to answer the new questions raised by their analysis.

First, it would be interesting to carry out the characterization described in this work for more pressure conditions (higher pressure conditions and without necessarily focusing on the 1-10 bars range). In this way it would be possible to compare the results obtained with the data available in the literature, where there is much more information about the CO_2 solubilization in bitumen at pressures above 2 Mpa. This characterization would in particular make it possible to further validate the experimental method used in this work, whereas the results in terms of maximum capacities would be less attractive with a view to long-term storage: as has been observed, although the increase in pressure in the solubilization phase leads to higher maximum capacities, when the samples are exposed to free air, they reach an equilibrium concentration independent of the CO_2 pressure initially used. Nevertheless, the use of higher pressures would allow to see if both formulations of bitumen follow the linear trend observed in this work, and if the asphalt aggregates do have a maximum saturation value between 0.1% and 0.2%.

It would also be interesting to perform the characterization at different temperature conditions, in this work only ambient temperature (20 °C) was used, and it would be interesting to assess how the solubilization capacity changes as temperature increases.

The characterization of the kinetics of solubilization at $P>P_{atm}$ has been realized only at 3 bars and 9 bars, it would therefore be interesting to carry it out also under different pressure conditions. In addition, the experimental points obtained at this stage are relatively few, due to the type of technique used that requires the opening and depressurization of the reactor. It would therefore be interesting to make a characterization with a greater number of experimental points, especially in the first hours of the process, but without disturbing the experimental environment. To do this, it would be necessary to provide for a mass measurement system integrated in the reactor or to change completely the measurement technique.

It would also be interesting to apply other types of models besides the Peleg model for the bitumen CO_2 solubilization process kinetics.

A detailed analysis of the asphalt Aggregates would allow to differentiate two theoretically co-present phenomena: the solubilization in the layer of bitumen covering the granular materials and the adsorption on the surface of the solid inert materials. In this work the results obtained show the presence of a weak and completely reversible adsorption phenomenon, and therefore there is no clear evidence of a long-term solubilization in the bitumen layer, perhaps because of the oxidation conditions of the latter.

The monitoring of the release of CO_2 has been carried out for relatively long times: over 200 hours (9 days), however, it would be necessary to further extend these times (several weeks or months) to verify whether the CO_2 storage, in the case of modified bitumen, is permanent as the models used suggest, or if there is a progressive release.

Another type of analysis that would integrate and complete the results obtained, is the GPC-MS (Gas Phase Chromatography - Mass Spectroscopy) of bitumen fumes obtained by heating the samples to temperatures up to 160°C, which would allow a more complete identification of the released components. Moreover, a more detailed characterization of the chemistry of the formulations investigated would allow to know which other types of volatile components released would be necessary to look for, besides the alkanes.

Finally, the chromatographic analysis was carried out on fumes obtained by heating bitumen samples subjected to a carbonation process at ambient pressure for one week. It would therefore be interesting to carry out the same analysis from bitumen samples which are not carbonated, or which have been subjected to pressure conditions above ambient pressure.

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7. Annexes

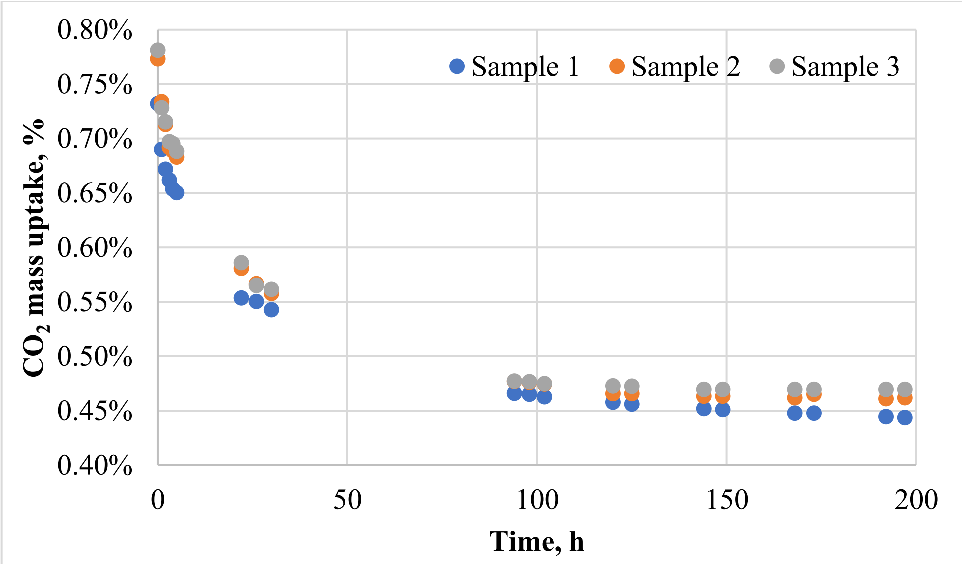

Figure 7.1: CO_2 mass uptake evolution over time for modified bitumen samples exposed to free air that have been originally exposed to a 1.5 bars CO_2 atmosphere.

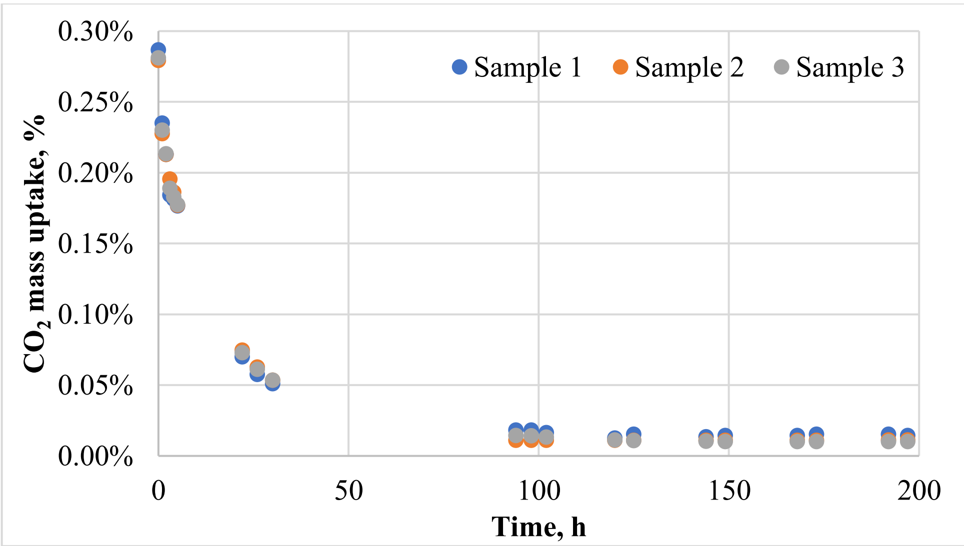

Figure 7.2: CO_2 mass uptake evolution over time for classic bitumen samples exposed to free air that have been originally exposed to a 1.5 bars CO_2 atmosphere.

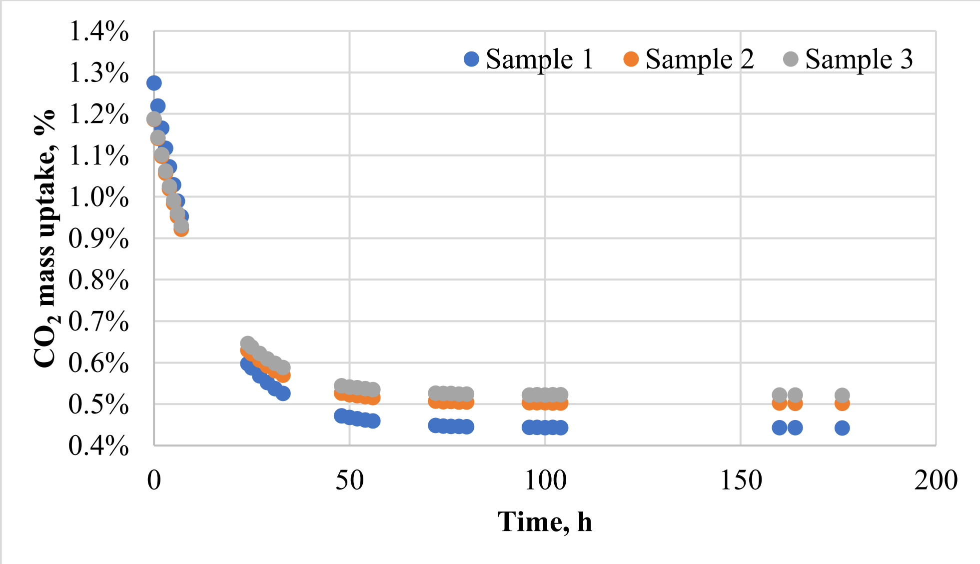

Figure 7.3: CO_2 mass uptake evolution over time for modified bitumen samples exposed to free air that have been originally exposed to a 5 bars CO_2 atmosphere.

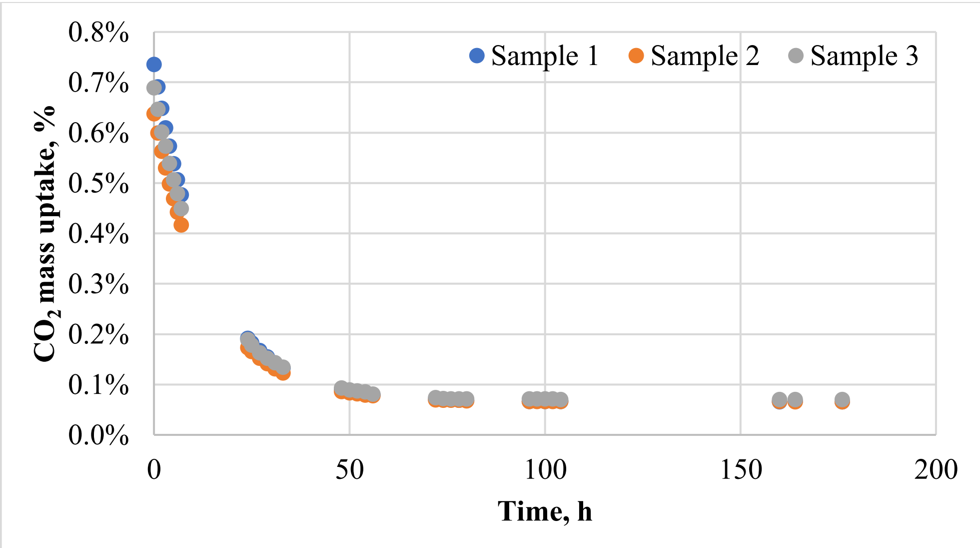

Figure 7.4: CO_2 mass uptake evolution over time for classic bitumen samples exposed to free air that have been originally exposed to a 5 bars CO_2 atmosphere.

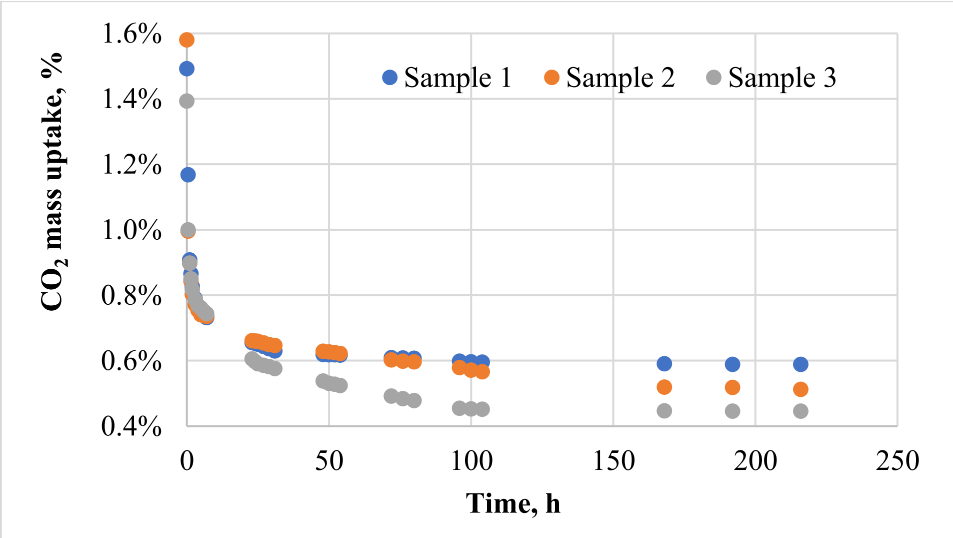

Figure 7.5: CO_2 mass uptake evolution over time for modified bitumen samples exposed to free air that have been originally exposed to a 7 bars CO_2 atmosphere.

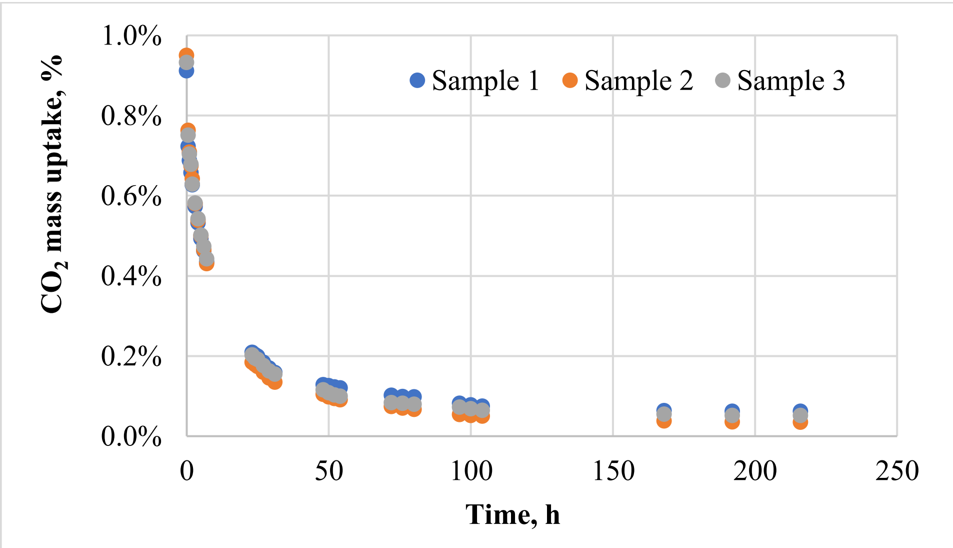

Figure 7.6: CO_2 mass uptake evolution over time for classic bitumen samples exposed to free air that have been originally exposed to a 7 bars CO_2 atmosphere.

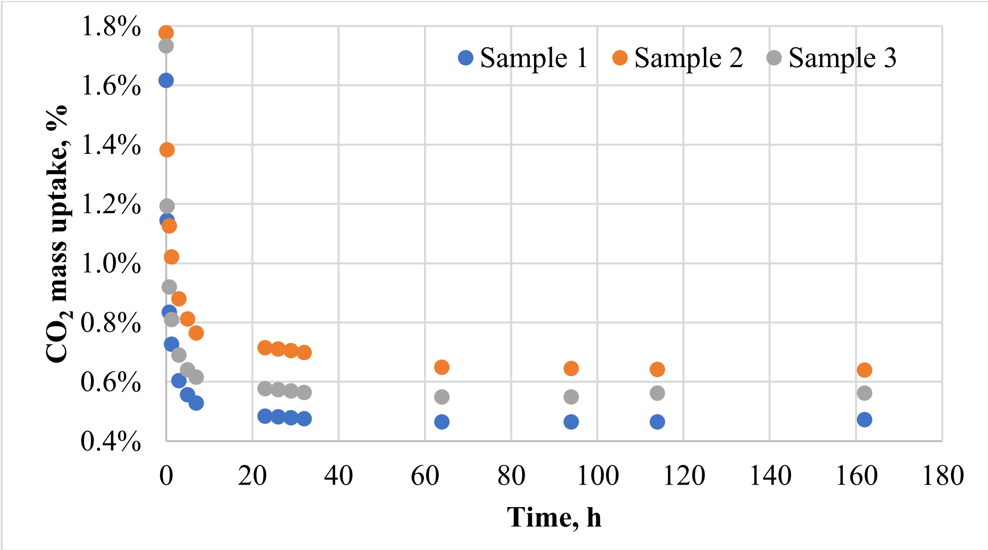

Figure 7.7: CO_2 mass uptake evolution over time for modified bitumen samples exposed to free air that have been originally exposed to a 9 bars CO_2 atmosphere.

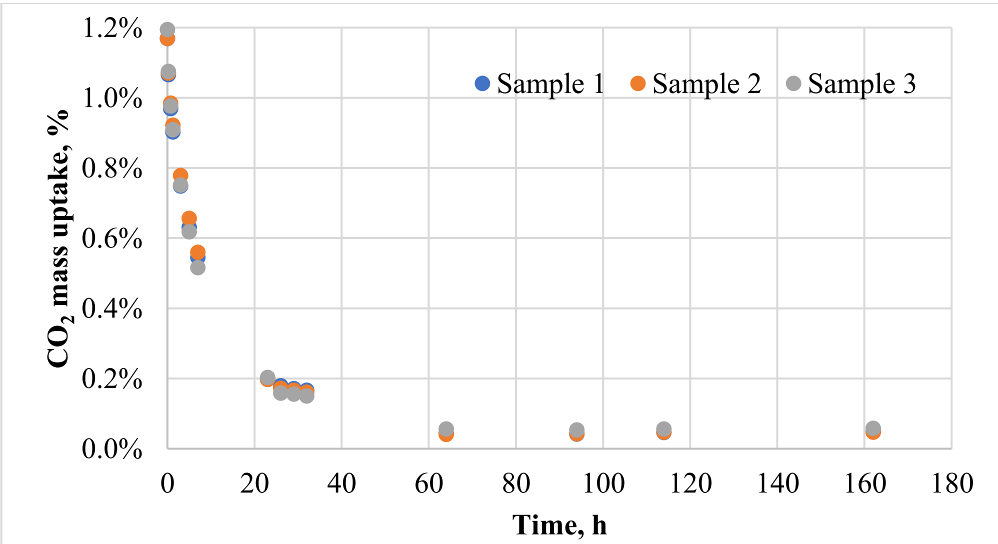

Figure 7.8: CO_2 mass uptake evolution over time for classic bitumen samples exposed to free air that have been originally exposed to a 9 bars CO_2 atmosphere.

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