EDGEWOOD
CHEMICAL BIOLOGICAL CENTER
U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

ECBC-TR-830

DECONTAMINATION EFFICACY OF CANDIDATE NANOCRYSTALLINE SORBENTS WITH COMPARISON TO SDS A-200 SORBENT: REACTIVITY AND CHEMICAL AGENT RESISTANT COATING PANEL TESTING

George W. Wagner

RESEARCH AND TECHNOLOGY DIRECTORATE

November 2010

20101208347

ABERDEEN PROVING GROUND, MD 21010-5424

Disclaimer

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* XX-11-2010	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* May 2008 - Oct 2008

4. TITLE AND SUBTITLE Decontamination Efficacy of Candidate Nanocrystalline Sorbents with Comparison to SDS A-200 Sorbent: Reactivity and Chemical Agent Resistant Coating Panel Testing	**5a. CONTRACT NUMBER** W911SR-07-C-0062
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Wagner, George W.	**5d. PROJECT NUMBER** 0714C
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ECBC, ATTN: RDCB-DRP-F, APG, MD 21010-5424	**8. PERFORMING ORGANIZATION REPORT NUMBER** ECBC-TR-830
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

Limited data from ECBC-TR-277 and ECBC-TR-302 are referenced herein per permission of NanoScale Corp. (Manhattan, KS) and the authors.

14. ABSTRACT-LIMIT 200 WORDS

Several nanocrystalline reactive sorbents, of varied particle size and surface area, were examined as decontaminating sorbents. The reaction kinetics of VX, GD, and HD were determined in addition to efficacy for surface decontamination of Chemical Agent Resistant Coating (CARC) paint. The Sorbent Decon System (SDS) A-200 sorbent was utilized as a control. The best sorbent for VX was nTiO_2, which enabled a half-life of <2 min. Comparable half-lives for GD (tens-of-minutes) were observed on nTiO_2, nMgO, and the commercial FAST-ACT® sorbent. Half-lives of a few to many hours were observed for HD on nAl_2O_3, nTiO_2, FAST-ACT®, and A-200, but only with sufficient surface hydration. Regarding reactivity only, A-200 did not perform as well as the nanocrystalline sorbents, especially for VX and GD. However, all of the sorbents, A-200 included, provided for the comparable removal of HD and GD from CARC panels, ca. 75 and 87%, respectively. An apparent surface-porosity of 0.8 cc/m^2 for the CARC paint is presumed responsible for this low efficacy. Smaller sorbent particle sizes (<5 μM) did not increase surface decontamination efficacy.

15. SUBJECT TERMS

Decontamination	A-200	VX	Reactive sorbents	HD
Nanocrystalline	CARC	GD	Surface decontamination	

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Sandra J. Johnson
a. REPORT U	**b. ABSTRACT** U	**c. THIS PAGE** U	UL	62	**19b. TELEPHONE NUMBER** *(include area code)* (410) 436-2914

Blank

EXECUTIVE SUMMARY

In a cooperative research and development agreement, the U.S. Army Edgewood Chemical Biological Center tested several of NanoScale Corporation's (Manhattan, KS) nanocrystalline reactive sorbents, of varied particle size and surface area, for decontamination efficacy of chemical agents. The currently-fielded Sorbent Decon System (SDS) A-200 sorbent was utilized as a control. Reaction kinetics with neat VX, GD, and HD were determined in addition to efficacy for the surface decontamination of Chemical Agent Resistant Coating (CARC) painted panels. For VX, the best sorbent was $nTiO_2$, which enabled a half-life for sorbed VX of less than 2 min. Comparable half-lives for GD (tens of minutes) were observed on $nTiO_2$, nMgO, and the commercial FAST-ACT® (NanoScale) sorbent. Half-lives of a few to many hours were observed for HD on nAl_2O_3, $nTiO_2$, FAST-ACT®, and A-200, but only with sufficient surface hydration. With regard to reactivity only, A-200 did not perform as well as the nanocrystalline sorbents, especially for VX and GD. However, all of the sorbents, A-200 included, provided for the comparable removal of HD and GD from CARC panels, ca. 75 and 87%, respectively. An apparent surface-porosity of 0.8 cc/m^2 for the CARC paint is presumed responsible for this low efficacy. Smaller sorbent particle sizes (>5 μm) did not increase surface decontamination efficacy for CARC paint, but did exhibit enhanced GD reactivity (even though they possessed lower surface area). High surface area favored VX reactivity. Reactivity for HD was not significantly enhanced by either small particle size or high surface area sorbent versions.

Blank

PREFACE

The work described in this report was authorized under cooperative research and development agreement Project No. 0714C and Contract No. W911SR-07-C-0062. The work was started in May 2008 and completed in October 2008.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Acknowledgments

The author thanks Nicole K. Fletcher and Tara L. Sewell for assistance with the chemical agent operations. Helpful discussions regarding Chemical Agent Resistant Coating panel testing with Lawrence R. Procell and Philip W. Bartram are gratefully acknowledged.

Blank

CONTENTS

APPENDIXES

FIGURE

TABLES

DECONTAMINATION EFFICACY OF CANDIDATE NANOCRYSTALLINE SORBENTS WITH COMPARISON TO SDS A-200 SORBENT: REACTIVITY AND CHEMICAL AGENT RESISTANT COATING PANEL TESTING

1. INTRODUCTION

The chemical warfare agents, VX, GD, and HD, have been well-known to sorb and react on metal oxides such as alumina for more than a decade.[1] Indeed, alumina is the active ingredient (A-200)[2] contained in the Sorbent Decontamination System (SDS).[3,4] Yet, compared to conventional metal oxides, nanosize metal oxides may afford enhanced reactivity owing to their larger surface areas, unusual exposed lattice planes, and greater proportions of highly-reactive edge and corner "defect" sites.[5,6] Thus, reactions of nanosize MgO, CaO, and alumina with VX, GD, and HD were undertaken.[7,8,9]

Bartram and Lynn[10,11] assessed the efficacy of a commercial, nanocrystalline MgO reactive sorbent, FAST-ACT®, and compared it to A-200. In the Phase I study,[10] the efficacy found for the decontamination of VX, GD, and HD on (unpainted) aluminum panels, is shown in Table 1. For the most part, except for GD at the highest 12.5 sorbent-to-agent ratio, Bartram and Lynn noted no significant difference between the two sorbents with regard to surface decon for the agents on unpainted aluminum (lower ratios studied showed non-significant difference for GD).

Table 1. Results of Bartram and Lynn[10] for the Decontamination of VX, GD, and HD on Unpainted Aluminum Panels[†]

Sorbent	Agent	Sorbent Applied (mg)	Sorbent:Agent Ratio	% Decon
FAST-ACT	VX	150	7.5	98.5
	GD	250	12.5	99.8
	HD	150	7.5	99.6
A-200	VX	150	7.5	98.1
	GD	250	12.5	99.5
	HD	150	7.5	99.8

[†] 2 in. diameter panels used. Contamination level 10 g/m^2. 15 min agent dwell time.[*] Three replicate panels.

---

[*] Per FM3-5, *NBC Decontamination*, DoA, Washington, DC, July 2000, immediate decontamination is expected to commence within 15 min following deposition of agent. Reaction rate for VX on FAST-ACT was 17 and 15 h vs. 31 and 17 h, and GD's reaction rate on FAST-ACT was 1.3 and 2.1 h vs. 4.1 and 21 h.

In Phase II, Bartram and Lynn[11] followed the reaction kinetics of VX, GD, and HD sorbed on FAST-ACT and A-200 by MAS NMR. They found that rubbing the agent into the sorbent significantly increased the decomposition of VX and GD, but not that of HD, and that the reaction rates of the agents were not significantly different on the two sorbents. These results are summarized in Table 2.

Table 2. Results of Bartram and Lynn[11] for the Reactions of VX, GD, and HD on FAST-ACT and A-200

Sorbent		VX $t_{1/2}$		GD $t_{1/2}$		HD $t_{1/2}$	
		Initial (min)	Final	Initial (min)	Final (h)	Initial	Final (h)
FAST-ACT	Normal[a]	14	17 h	12	1.3	1.1 h	31
		13	15 h	20	2.1	32 min	25
	Rubbed[b]	11	41 min	<5[c]	–	1.6 h	26
		<5[c]	–	<4[c]	–	1.8 h	12
A-200	Normal[a]	23	31 h	13	4.1	1.4 h	19
		10	17 h	8.2	21.0	1.0 h	16
	Rubbed[b]	<5[c]	–	<4[c]	–	45 min	19
		<4[c]	–	<4[c]	–	19 min	20

[a] 4–6 µL agent added to 200–300 mg FAST-ACT or 2–3 µL added to ca. 100 mg A-200 without rubbing or agitation.

[b] 200–300 mg FAST-ACT rubbed onto 6 µL agent or 100–300 mg A-200 rubbed onto 4–6 µL agent contained on unpainted alumina panels.

[c] Agent not detected, upper-limit $t_{1/2}$ estimated from first time point.

Davis et al.[4] performed A-200 decontamination efficacy testing for VX, TGD, and HD on a variety of surfaces, including Chemical Agent Resistant Coating (CARC) paint; data for the latter surface are shown in Table 3.

Table 3. Results of Davis et al.[4] for the Decontamination of VX, TGD, and HD on CARC-Painted Steel Panels by A-200 at 25 °C*

Agent	CARC (%)	Bare Stainless Steel (%)	Recovery Efficiency from Stainless Steel (%)
VX	97.6	98.0	51.7
TGD	72.6	99.1	100.0
HD	94.9	99.8	71.0

[*] 7 cm diameter panels contaminated with 10 g/m^2 agent. No agent dwell time. 5 min sorbent decontamination time. Three replicate panels.

These results require further comment because of the complicated nature of the CARC surface, which is known to be penetrated and softened by the agents.[12] Thus, owing to sorption of agent into CARC, time is of the essence for its decontamination. The longer one waits, the smaller is the amount of agent remaining on or near the surface that can be easily removed, especially by a non-penetrating decontaminant such as a solid sorbent. The order of penetrating/softening ability of the agents is HD >> VX > GD;[12] therefore, HD tends to be the most difficult to remove or decon on CARC, followed by VX; GD is by far the easiest.

However, the situation changes for thickened GD (TGD) owing to the need to adequately dissolve or otherwise remove the sticky substance from the surface. This is especially problematic for CARC due to its dull, matte-finish. Thus, the surface roughness would tend to cling and grab onto thickened agents more so than a smooth metal or glass surface.

These effects are certainly evident in the results in Table 3 where, considering the simple liquid agents, less HD (94.9%) is able to be removed from the CARC surface than VX (97.6%). The low removal of TGD (72.6%) is undoubtedly due to its oozing into the rough-surface of CARC and the inability of the A-200 sorbent to quickly sorb this viscous, thickened agent. Indeed, on bare (smooth) stainless steel, TGD removal jumps to 99.1%. It is important to further note that the removal efficiency of VX, and especially that of HD, would be considerably less had a non-zero (i.e., 15 min) dwell time been employed. The results for TGD would probably not be so affected by a finite dwell time as the presence of the thickener tends to slow the sorption of agent into a susceptible surface.[12] Finally, the low recoveries of VX and HD from the stainless steel surface (51.7 and 71.0%, respectively) is probably due to agent running-off the edge of the coupon (as previously noted by Bartram and Lynn).[10] This tends to not be a problem for TGD, which flows very slowly; thus, the recovery of 100%.

It is the aim of the present study to examine several nanocrystalline materials to determine if they are superior to FAST-ACT and to compare them to the performance of A-200. Basically, a decontamination sorbent can excel in one or two ways: 1) quickly react with/destroy sorbed agent (kinetics) and 2) remove/sorb agent from surfaces to lowest possible levels. Some of the individual sorbents have been varied in terms of particle size and surface area to determine what impact, if any, these attributes have on reaction kinetics and removal efficiency.

To give the candidate sorbents a chance to demonstrate clear superiority, purposely-challenging tests were undertaken. The first test, performed by MAS NMR, assesses the ability of a sorbent to react with a single, 5 μL drop of agent without rubbing or any external agitation. The rationale for this is that such rubbing or agitation would indeed improve any innate reactivity (as demonstrated by Bartram and Lynn)[11] but that a sorbent that can function without rubbing or mixing is clearly superior to one that cannot. The second test assesses the ability of a sorbent to decontaminate CARC paint using the 15 min dwell time mentioned above for the immediate decontamination scenario. Thus, a sorbent whose particles are most adept at slipping into micro-cracks and crevices of non-smooth surfaces to ferret out and sorb micro-pools of agent will exhibit the best efficacy. Finally, the ability of a sorbent to remain efficacious in air (air-stability) was assessed by repeating the reactivity test following 24 h exposure of the sorbent to air.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Sorbent samples were received from NanoScale Corporation (Manhattan, KS) in sealed plastic jars containing ~1 g. The sorbents were either used as-received or subjected to 24 h air-exposure (see below). For the as-received material, air-exposure was limited by opening a fresh jar just prior to each experiment.

Initially, the following five sorbents were examined:

1. NanoActive® Magnesium Oxide Plus, lot # 01-0105 (nMgO #1)
2. NanoActive Magnesium Oxide, lot # 02-0254 (nMgO #2)
3. NanoActive Titanium Oxide, lot # 12-0160 (nTiO_2 #1)
4. NanoActive Aluminum Oxide Plus, lot # 08-0133 (nAl_2O_3)
5. Guild Alumina (A-200)

The following four sorbents were then additionally examined:

1. NanoActive TiO_2 2, lot #1207310801 (nTiO_2 #2)
2. Modified Magnesium Oxide Plus, lot # 01061908B1 (nMgO #3)
3. FAST-ACT, lot # 15-0166
4. FAST-ACT 2, lot # 1508080801

The properties of the above materials are listed in Table 4.

Table 4. Particle Size and Surface Area of Studied Samples

Sample	Particle Size Distribution (Volume %)				Surface Area
	<5μm	5-20μm	20-50μ	>50μm	m2/g
nMgO #1	7.65	53.51	37.40	1.44	718
nMgO #2	23.84	60.70	14.63	0.84	241
nTiO$_2$ #1	28.08	28.02	15.55	28.35	489
nAl$_2$O$_3$	90.34	8.45	1.21	0.00	304
nTiO$_2$ #2	13.79	28.56	50.60	7.06	492
MgO #3	0.00	33.17	60.54	6.28	771
FAST-ACT	27.93	53.53	10.31	8.23	326
FAST-ACT 2	8.36	29.50	55.81	6.33	659
A-200	4.07	12.41	51.70	31.82	312

2.2 Air-Exposure

To assess the sensitivity of the sorbents to air, ca. 0.5 g samples of each sorbent was spread onto a piece of weighing paper and allowed to stand for 24 h in air. The weight gain was measured and the exposed sample was subjected to a second agent reactivity test to compare its performance with the fresh, as-received material.

2.3 Reactivity Testing

Reactivity testing was done by MAS NMR using Varian INOVA 400 or Unityplus 300 NMR spectrometers equipped with Doty Scientific 7 mm MAS probes. In a typical experiment, a 10 μL syringe was used to inject 5 μL neat liquid agent into the middle of a column of sorbent contained in a 7 mm MAS NMR rotor (Doty Scientific). The rotor was sealed with double o-ring endcaps and spectra were taken periodically to monitor the reaction progress and identify products. ^{13}C-labeled HD (HD*) was employed to enhance sensitivity as these reactions were monitored by ^{13}C MAS NMR. ^{31}P MAS NMR was employed to monitor the reactions of VX and GD. Spectra were referenced to TMS (0 ppm, ^{13}C) and 85% H_3PO_4 (0 ppm, ^{31}P).

2.4 Panel Testing

Two inch diameter CARC-painted aluminum coupons were employed (area = 20 cm^2). Six replicate panels were employed for each test. Twenty milligrams of agent (10 g/m^2) was deposited onto each panel by applying 16 μL HD (d = 1.27 g/cm^3) or 20 μL VX or GD (both d = 1.0 g/cm^3) in ca. 2 μL drops. The drops were then manually spread across each panel using a piece of parafilm to ensure uniform surface coverage. The panels were covered with an inverted Petri dish (to prevent undue evaporation of agent) and allowed to stand for 15 min.

At the end of the 15 min agent dwell period, 200 mg of pre-weighed, candidate sorbent was emptied from a 4 mL screw cap vial onto each panel and evenly-distributed across the panel with a microspatula. Then a 1 kg 2 in. diameter weight covered with aluminum foil on the bottom was used in the manner of Bartram and Lynn[10] to rub the sorbent on each panel: five clockwise turns followed by five counterclockwise turns. This process took 1 min or less. Some excess sorbent was ejected over the side of the panel during the rubbing process. The remaining excess sorbent was immediately scraped off with a micro spatula; however, a fine coating of powder still invariably clung to the rough CARC surface. No additional action was taken to remove this fine coating, which would also certainly remain on treated CARC surfaces in the field.

To assess the amount of agent remaining, a contact test was first employed: each panel was placed on a 30 °C slide warmer (to simulate being touched by a warm, bare hand) and a 2 in. latex (Dental Dam) disk was placed on top of each panel, followed by a 2 in. aluminum foil cover (to prevent agent from migrating past the latex). A 1 kg weight was placed on top of the aluminum foil cover to exert pressure during a contact period of 15 min. At the end of the 15 min contact period, the latex and foil disks were removed from each panel and extracted in 20 mL chloroform for 1 h. The panel itself was then extracted in a covered weighing dish with 10 mL chloroform, also for 1 h, to determine the residual agent hazard. The extracts were analyzed by ^{1}H and/or ^{31}P NMR to determine the amount of agent present.

3. RESULTS AND DISCUSSION

3.1 Reactivity Testing

Observed half-lives for 5 μL VX, GD, and HD added to the fresh, as-received sorbents and the 24 h air-exposed materials are given in Table 5 (raw kinetic data and select MAS NMR spectra Appendices A and B). Owing to previously noted diffusion effects,[7] some reactions exhibited an initial fast reaction followed by a much slower, diffusion-limited reaction; thus, in these instances, separate half-lives are reported for the two regimes.

3.1.1 nMgO Sorbents

For the nMgO sorbents, GD tended to react quickest with half-lives on the order of tens of minutes. That the GD reactions did not exhibit severe diffusion limitations can be ascribed to both its rather high volatility (compared to VX and HD) and good water solubility (GD is soluble in water, but not miscible), the latter attribute presumably allowing it to dissolve and diffuse within surface-bound water layers. Note, however, that despite air-exposure and the attendant potential water adsorption, some degradation of the GD reactivity occurred. This is easily understood by the observation that the nMgO sorbents tended to gain the most weight upon air-exposure (upwards of 30%) and that ^{13}C MAS NMR (spectra B5-6 in Appendix B) showed the formation of carbonate ($CO_3^{=}$) on this material as a result of reaction with ambient CO_2 in the air. Such a process would tend to neutralize the very basic MgO surface; thus, the deleterious effect on GD hydrolysis. Note that carbonate was not detected on any of the fresh nMgO (spectra B5-7 in Appendix B), which is consistent with good quality control during their manufacture and packaging to avoid undue air-exposure.

VX also tended to react more quickly with fresh nMgO (half-life on the order of hours) and did not appear to be severely diffusion-limited on nMgO #1, perhaps as a result of spontaneous wetting of this particular nMgO. However, air-exposure did cause a major loss in observed VX reactivity/diffusion. In its protonated state, VX is water soluble. However, with a pK_a of 8.6,[13] VX is most likely "free-based" by the basic MgO surface into the unprotonated state; thus, it would suffer limited water solubility and, hence, diffusion (barring spontaneous wetting), within surface water layers.

For HD on nMgO, the reaction appears entirely diffusion-limited (in no small part due to its water insolubility) - there is no fast, initial reaction. Yet, consistent with the very basic nMgO surface, the major reaction mechanism for HD is elimination to its vinyl and divinyl products, varying from 50% on nMgO #1 to 67% on nMgO #2 and >90% on nMgO #3 (the latter material evidently possesses the highest basicity). Of course, as a result of the aforementioned carbonation/neutralization of surface basicity, elimination is curtailed in the air-exposed samples to <10% in nMgO #1 and 50% in nMgO #2, and the overall reactivity suffers. It is further interesting to note that air-exposure resulted in greater carbonation of nMgO #2 compared to nMgO #1 (as indicated by their ^{13}C MAS NMR spectra, B6 and B5, respectively, Appendix B) which is consistent with the former's higher apparent basicity. Presumably, the highest basicity nMgO #3 would have suffered the most carbonation, but it was not tested.

Regarding the varied particle size and surface area of the nMgO sorbents studied, GD tended to react quickest with the fresh sorbent possessing the smaller particle size distribution and lower surface area, nMgO #2. However, upon air-exposure, nMgO #1 was able to retain its reactivity better. That this is so is perhaps related to its larger particle size, which would tend to react slower with ambient CO_2. This is consistent with the somewhat lower weight gain of the nMgO #2 sorbent during 24 h air-exposure, 25-26 wt % vs. 28-30 wt% for nMgO #1. HD tended to react equally well with the two fresh materials, but, again, the larger-particle material tended to retain its reactivity better during 24 h air-exposure. As for VX, it tended to react better with the larger-particle size, higher-surface area nMgO #1, even after 24 h air-exposure.

Table 5. Half-Lives for VX, GD, and HD Added to Candidate Sorbents

Sorbent	Treatment	VX	GD	HD (h)
nMgO #1	fresh	4.2 h	24 min	15
	air-exposed	9.3/43 h	28 min	24
nMgO #2	fresh	1.3/11 h	15 min	15
	air-exposed	53 h	47 min	35
nMgO #3	fresh	not done	not done	2.3/24
	air-exposed	not done	not done	not done
nTiO_2 #1	fresh	23 min (run 1)	2.8 h	5.4/17
		23 min (run 2)		
	air-exposed	<2 min (run 1)	29 min	1.5/11
		<2 min (run 2)		
nTiO_2 #2	fresh	36 min	17 min/1.3 h	1.5/31
	air-exposed	8.5 min	9.3 min/23 min	1.5/10
nAl_2O_3	fresh	2.1/32 h	3.0 h	6.3/34
	air-exposed	2.8/31 h	2.0 h	5.7
FAST-ACT	fresh	41 min/2.2 h	16 min	4.0/38
	air-exposed	26 min/3.9 h	34 min	4.3/14
FAST-ACT2	fresh	55 min/3.3 h	1.2 h	3.4/28
	air-exposed	1.5 h	24 min	2.2/13
A-200	fresh	7.4/56 h	1.6/13 h	29
	air-exposed	14/54 h	4.0 h	19

3.1.2 nTiO_2

Although VX may be unprotonated and, thus, possess limited water solubility within surface water layers on nMgO, this is obviously not the case for nTiO_2 where the half-life for VX is an astoundingly short 23 min. Moreover, upon air-exposure, nTiO_2 picks up 13–16% water, further enhancing VX diffusion and reaction such that the half life is unbelievably under 2 min! Such fast VX reactions, where an apparently non-diffusion limited half-life of <30 min occurs, has previously been seen on nanotubular titania (NTT).[14] It is known that the surface hydroxyls[15] of titania (and NTT[16]) are more acidic than MgO, and even Al_2O_3 (basic enough to eliminate HD),[9] thus accounting for the presumed VX protonation and facilitated diffusion (especially when sufficient hydration layers are present) on nTiO_2 (and NTT). That the VX half-lives are a bit longer on nTiO_2 #2 could be due to fortuitous differences in water content; for example, upon air-exposure, it picked up only 15.6% weight compared to 20.8% for nTiO_2 #1. The effect of sufficient hydration layers on (water-soluble) agent diffusion is also apparent in the significantly shorter half-life of GD (29 min) on air-exposed nTiO_2 #1 compared to the fresh material (2.8 h). For nTiO_2 #2, the behavior of GD is quite different in that, following an initially fast reaction, a diffusion-controlled reaction ensues (albeit still at a faster rate than on nTiO_2 #1). It is not clear if these differences are due to particle morphology, surface characteristics, or hydration effects. However, the HD results suggest that nTiO_2 #1 has the highest initial water content as its hydrolysis is fastest on this as received material. But after air-exposure both nTiO_2 formulations possess virtually indistinguishable HD-reaction behavior.

Like nMgO, GD tended to react best with the smaller-particle $nTiO_2$ #2, before and after 24 h air-exposure. Also like nMgO, VX conversely reacted best with the larger-particle $nTiO_2$ #1, before and after 24 h air-exposure. Both materials possessed identical surface areas. Again, HD did not appear to favor one material better than the other.

3.1.3 nAl_2O_3 and A-200

For HD on nAl_2O_3, the air-exposed sample only picks up 1–6% water but this is evidently enough to reduce the (diffusion-limited) half-life from 34 to 5.7 h—the shortest sustained half-life for HD observed on any of the sorbents. Besides hydrolysis, similar but minor amounts of HD elimination products are observed on both fresh and air-exposed material (surface carbonation of the most basic sites does not seem to occur as it does with nMgO). The GD half-life is similarly reduced from 3 to 2 h (yet still slower than on the more basic nMgO surface). But for VX there is virtually no change; it is extremely persistent on both dry and hydrated materials. The reason for the persistency of VX on alumina, and MgO, for that matter, can be attributed to the tight binding of its hydrolysis product EMPA to these basic surfaces (as detected by ^{31}P MAS NMR);[7,9] thus, EMPA is unable to assume its usual role to autocatalytically hydrolyze VX.[13] EMPA does not bind tightly to the $nTiO_2$ (nor to the NTT[14]) surface, so it remains free to dismantle VX with aplomb.

These observations for nAl_2O_3 also apply to A-200 which tends to pick up even less water upon air-exposure (1–2%). In a similar manner, VX also remains persistent on both the fresh and air-exposed materials as EMPA is still sidelined. However, the half-life for GD is considerably reduced on the air-exposed sample from 13 (diffusion-limited) to 4 h as a result of simply picking up 1.8% water. Modest gain is also seen for HD reactivity on the slightly wetter material, reducing its half-life from 29 to 19 h. As with nAl_2O_3, quite similar but minor amounts of elimination products are observed on both fresh and wet materials.

3.1.4 FAST-ACT and FAST-ACT 2

VX reacts rather well with both FAST-ACT and FAST-ACT 2, even after air-exposure, as half-lives do not exceed a few hours. GD gives mixed results, having the shortest half-life on fresh FAST-ACT (16 min), which effectively doubles on the air-exposed material (34 min) whereas on FAST-ACT 2 the half-life is shorter on the air-exposed (24 min) and quite long on the fresh (1.2 h) material. HD shows its typically slow, water-starved reactivity on the dry, fresh sorbents (unlike nMgO, only minor elimination of HD occurs) whereas enhancement occurs for the air-exposed, hydrated materials. Typical weight gains are 18–24% and 22–30% for air-exposed FAST-ACT and FAST-ACT 2, respectively.

Like nMgO, GD reacted best with the fresh, smaller-particle size, lower-surface area FAST-ACT, whereas the larger-particle, higher-surface area FAST-ACT2 maintained its reactivity (actually improving). Also like nMgO, HD reacted similarly with both particle sizes. However, unlike nMgO, VX tended to react better with the smaller-particle size, smaller-surface area FAST-ACT.

3.1.5 Reactivity Testing Summary

From the reactivity results it is easy to see that $nTiO_2$ has the most potential to afford quick, simultaneous reactivity for all three agents, provided sufficient water is present. Although current water levels of 16–21% are effective at reducing the VX and GD half-lives to <2 and 29 min, respectively, the HD half-life is still 11 h, nearly twice as long as that of air-exposed nAl_2O_3 (5.7 h). However, perhaps even higher water levels could achieve further reduction in the HD half-life while maintaining, or even further enhancing, its unprecedented VX and GD reactivity.

With regard to particle size and/or surface area, the smaller particle size versions of nMgO, $nTiO_2$, and FAST-ACT tended to react fastest with GD, even those with reduced surface areas. Conversely, VX reacted best with higher-surface area nMgO, FAST-ACT, and larger-particle size $nTiO_2$. However, for HD, no pronounced particle size and/or surface area effects could be discerned.

Overall, nano-based sorbents were highly superior to A-200, having much shorter half-lives, with $nTiO_2$ being the most effective. The shortest, sustained half-lives observed for the agents on the sorbents, either provided by fresh or air-exposed materials, are collected in Table 6.

Table 6. Shortest, Sustained Half-Lives Exhibited by Sorbents,
Fresh or Air-Exposed, for VX, GD, and HD

Agent	nMgO	$nTiO_2$	nAl_2O_3 (h)	FAST-ACT	A-200 (h)
VX	4.2 h[a]	<2 min[b]	31.0[c]	1.5 h[d]	54.0[c]
GD	15 min[e]	23 min[f]	2.0[c]	16 min[g]	4.0[c]
HD	15 h[a,e]	11 h[b]	5.7[c]	13 h[d]	19.0[c]

[a] Fresh nMgO #1.
[b] Air-Exposed $nTiO_2$ #1.
[c] Air-Exposed material.
[d] Air-Exposed FAST-ACT2.
[e] Fresh nMgO #2.
[f] Air-Exposed $nTiO_2$ #2.
[g] Fresh FAST-ACT.

From the shortest, sustained half-lives given in Table 6, rankings of the sorbents with regard to their ability to react with VX, GD, and HD in the most expeditious manner can be gleaned. These rankings are shown in Table 7 where half-lives of the same order-of-magnitude are considered equivalent (minutes > tens of minutes > hours > tens of hours). Note that, at present, these rankings should be considered tentative as a comprehensive study of the effect of water-content on the reaction kinetics, which dramatically impacts the observed half-lives (see above), has not been done. Nevertheless, this ranking suggests $nTiO_2$ as the sorbent possessing the most potential to provide simultaneous, fast reaction with all three agents, because its efficacy is by far the best for VX; comparable to nMgO and FAST-ACT for GD; and reasonably close to that of nAl_2O_3 for HD. Moreover, unlike nMgO, $nTiO_2$ is not deactivated by air (see above), rendering it a more robust choice for use as a reactive sorbent.

Table 7. Sorbent Reactivity Ranking Based on Observed Agent Half-Lives

VX	$nTiO_2 >> FAST\text{-}ACT \approx nMgO > nAl_2O_3 \geq A\text{-}200$
GD	$nMgO \approx FAST\text{-}ACT \approx nTiO_2 > nAl_2O_3 > A\text{-}200$
HD	$nAl_2O_3 \geq nTiO_2 \approx nMgO \approx FAST\text{-}ACT \approx A\text{-}200$

3.2 Panel Testing

Results for the decontamination of HD and GD on CARC panels are given in Table 8. Average values and standard deviations are shown for the six-panel replicates. Complete data sets are given in Appendix C. Illustration of the contact and residual hazard (extract) tests are shown in the following Figure.

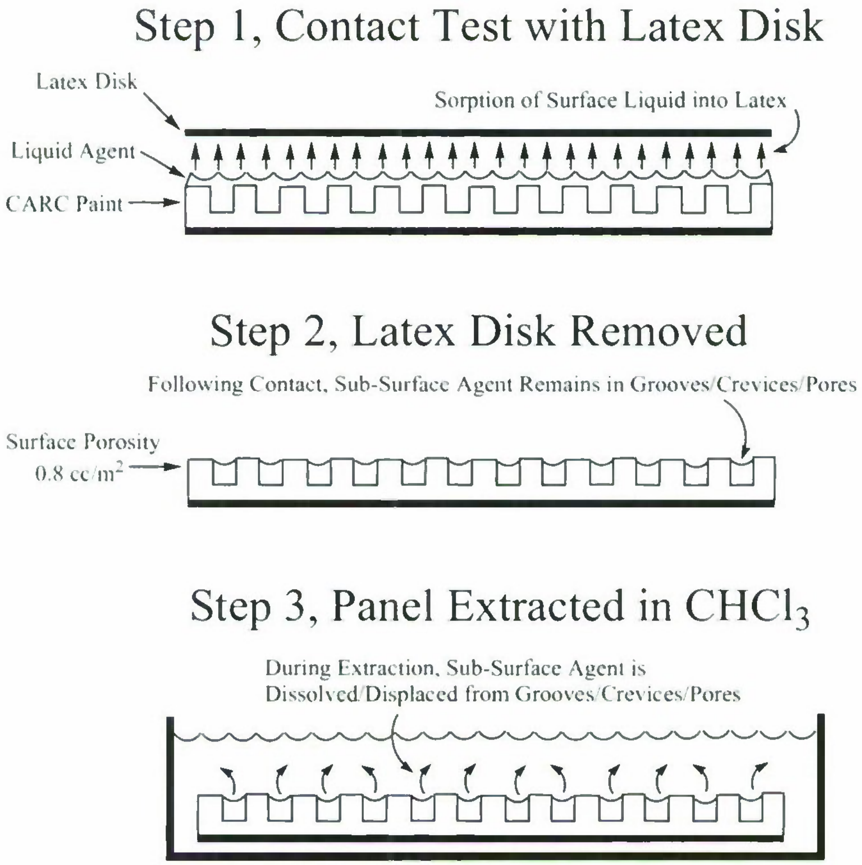

Figure. Illustrations of Contact and Hazard Tests to Determine Residual Agent Present on CARC Panels. For blank runs (no sorbent decon), the amount of HD and GD remaining following the contact test was identical (1.6 μL) indicating a surface porosity of about 0.8 cc/m^2 for the CARC panels as depicted.

As mentioned in the Introduction, the 15 min agent dwell time has rendered HD noticeably more difficult to decontaminate on the CARC panels, so that only 69 to 77% can be removed compared to 86–87% for the much less penetrating/softening GD. From the

HD % Decon results it appears that the nMgO #1 sorbent (69%) may perhaps be slightly less effective than nMgO #2 (74%), $nTiO_2$ (75%), and nAl_2O_3 (76%), all of which, considering the standard deviation, provide virtually identical results to that of the A-200 (77%).

Table 8. Panel Test Results for Sorbent Decontamination of CARC Paint[a]

	HD				GD			
Sorbent	Contact	Residual	Total	% Decon	Contact	Residual	Total	% Decon
nMgO #1	1.8 (0.45)	2.4 (0.14)	4.2 (0.59)	74 (3.8)	1.7 (0.52)	0.95 (0.23)	2.6 (0.36)	87 (1.6)
nMgO #2	2.5 (0.21)	2.4 (0.23)	4.9 (0.40)	69 (3.8)	1.4 (0.46)	1.2 (0.17)	2.8 (0.39)	86 (2.0)
$nTiO_2$ #1	2.0 (0.56)	1.9[b] (0.35)	4.0[b] (0.70)	75[b] (4.4)	1.4 (0.098)	1.2 (0.27)	2.6 (0.23)	87 (1.2)
nAl_2O_3	2.5 (0.30)	1.4 (0.16)	3.9 (0.41)	76 (2.4)	1.2 (0.26)	1.4 (0.16)	2.6 (0.15)	87 (0.75)
A-200	2.5 (0.44)	1.3 (0.46)	3.8 (0.47)	77 (2.9)	2.0 (0.24)	0.65 (0.093)	2.6 (0.24)	87 (1.0)
No Decon Control[c]	14 (1.5)	1.6 (0.36)	16 (1.2)	98 (9.3)	12 (1.0)	1.6 (0.50)	13 (1.2)	66 (5.8)

[a] 2 in. diameter panels contaminated with $10\ g/m^2$ agent. 16 μg HD or 20 μg GD manually spread evenly across panel. 15 min agent dwell time. 5 min sorbent decontamination time. Units in micrograms ([μg] agent recovered). % Decon is the total percent agent removed from panel. Six replicate panels. Standard deviation shown in parentheses.

[b] Average of three replicates.

[c] No sorbent applied (to determine agent recovery efficiency).

Regarding particle size and the potential ability of smaller particles to venture into the presumed small crevices and clefts of the rough CARC surface, nAl_2O_3 possesses the highest fraction of the smallest, <5 μm particles (90.34%), yet was statistically no better at removing imbedded HD or GD than A-200, which possesses the lowest fraction of these small particles (4.07%). The only hint of a particle-size effect for agent removal is given by the marginally-better performance of nMgO #2 compared to nMgO #1, whose fractions of <5 μm particles are 23.84 and 7.65%, respectively; however, their % Decon, 69 and 74%, are still within experimental error (±3.8%). Thus, either the surface features of CARC within which agent abides have openings significantly-smaller than 5 μm, or the sorbent particles able to reach the secreted agent renders insignificant reaction/decontamination on the required time-scale (15 min). However, whatever the reason, small particles (<5 μm) of the current materials do not appear to enhance the surface decontamination efficacy of CARC paint.

It is important to note that for the control experiment, the excellent recovery of HD from the CARC panels (98%, in the absence of applied sorbent) shows that the 1 h $CHCl_3$ extraction procedure is sufficient to recover the CARC-sorbed HD. For the GD control experiment, noticeable loss occurred as some of the GD ran over the sides of the panel during the

15 min dwell time; thus, explaining the low GD recovery of only 66%. It is further interesting to note that the extracts of both the GD and HD controls are identical, 1.6 µL. Thus, the same amount of liquid remained entrained and inaccessible to be sorbed by the latex disk during the 15 min contact hazard assessment period (see Figure). This observation suggests that the CARC paint possesses a large porosity of about 0.8 cc/m^2 as depicted in the Figure.

For GD, all the sorbents performed identically. Thus, the panel testing provided little insight into the true potential of the candidate sorbents to fully function as effective decontaminants, to both sorb agent from surfaces *and* to quickly react with them to complete the decontamination. It is primarily due to the rather consistent panel test results across the sorbent candidates that VX panel testing was not done; rather, time and funds were used to do the additional reactivity testing for the second batch of sorbent candidates.

Regarding the results of Davis et al.,[4] the A-200 sorbent was able to achieve 94.9% removal of HD from their CARC test panels. This high value is certainly due, at least in part, to the zero agent dwell time employed, i.e., the HD did not have a chance to penetrate/sorb into the CARC paint. However, another contributing factor could be the true HD resistance of the actual CARC paint employed as the resistance of different CARC lots to HD penetration/softening varies widely. Therefore, for CARC panel testing, in particular, it is important to always employ a control decontaminant so that the *relative* effectiveness of decontaminates can be determined with respect to the control, rather than attempting to rely solely on *absolute* decontamination levels obtained by experimental methods employing different agent dwell times and/or CARC surfaces of varying pedigree.

4. CONCLUSIONS

The reactivity testing revealed that nTiO_2, by far, possesses the fastest reaction with VX (half-life <2 min) of any of the other candidates and its reaction rate with GD is comparable to that of nMgO and FAST-ACT (half-lives of tens of minutes). However, this fast rate is only seen when nTiO_2 is sufficiently hydrated. Hydration of nTiO_2 also increases the reaction rates of GD and HD. Yet, the HD half-life on hydrated nTiO_2 is still on the order of several hours, comparable, but still nearly twice as long as that of hydrated nAl_2O_3. Thus, the full hydration regime of these two sorbents should be explored to determine which actually provides the best HD reactivity.

The panel test results for HD and GD did not enable a clear distinction of the potential efficacy of the sorbent candidates as all tended to provide for nearly identical removal of HD from the Chemical Agent Resistant Coating (CARC) panels (VX panel testing was not done because of this). However, for HD, it did appear that nMgO #1, at 69% removal, did not function quite as well as nMgO #2 (74%), nTiO_2 (75%), nAl_2O_3 (76%), and A-200 (77%), the latter sorbents performing identically within experimental error. For GD, all the sorbents achieved 87% removal of this agent from CARC.

Finally, regarding particle size and surface area of the sorbents, small particles tended to provide for the fastest GD reactions whereas higher surface areas and/or larger particle sizes tended to favor VX reaction. The reaction of HD was quite insensitive to either particle size or surface area, tending to not favor one over the other. For surface decontamination of CARC paint, smaller particle sizes, even those under 5 µm, did not significantly improve the removal/reaction/decontamination of GD or HD imbedded within the rough paint surface. Based on the ability of contact hazard testing to remove surface-sorbed agent, the CARC paint appeared to possess a substantial surface-porosity of about 0.8 cc/m^2.

LITERATURE CITED

1. Bartram, P.W.; Wagner, G.W. Decontamination of Chemical Warfare Agents Using Activated Aluminum Oxide. U.S. Patent 5,689,038, Nov. 18, 1997.

2. MSDS for A-200-SiC-1005S; Guild Associates, Dublin, OH.

3. Friday, D.K.; Rossin, J.A.; Fitzgerald, G.; Meams, H. *Sizing and Timing Trial Test Report for M295 MITT on Development of Sorbent for Immediate Decontamination*; ECBC-CR-057; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2002; UNCLASSIFIED Report (AD-B276 882).

4. Davis, W.G.; Kewan, A.; Cao, T.D.; Spackman, T. *Formal Test Report for the XM100 Sorbent Decontamination System (SDS). Decontamination Laboratory Testing*; WDTC-TR-01-037; U.S. Army Dugway Proving Ground: Dugway, UT, 2002; UNCLASSIFIED Report.

5. Klabunde, K.J.; Stark, J.; Koper, O.; Mohs, C.; Park, D.G.; Decker, S.; Jiang, Y.; Lagadic, I.; Zhang, D. Nanocrystals as Stoichiometric Reagents with Unique Surface Chemistry. *J. Phys. Chem.* **1996**, *100*, 12142–12153.

6. Stark, J.V.; Park, D.G.; Lagadic, I.; Klabunde, K.J. Nanoscale Metal Oxide Particles/Clusters as Chemical Reagents. Unique Surface Chemistry on Magnesium Oxide As Shown by Enhanced Adsorption of Acid Gases (Sulfur Dioxide and Carbon Dioxide) and Pressure Dependence. *Chem. Mater.* **1996**, *8*, 1904–1912.

7. Wagner, G.W.; Bartram, P.W.; Koper, O.; Klabunde, K.J. Reactions of VX, GD, and HD with Nanosize MgO. *J. Phys. Chem. B* **1999**, *103*, 3225–3228.

8. Wagner, G.W.; Koper, O.B.; Lucas, E.; Decker, S.; Klabunde, K.J. Reactions of VX, GD, and HD with Nanosize CaO: Autocatalytic Dehydrohalogenation of HD. *J. Phys. Chem. B* **2000**, *104*, 5118–5123.

9. Wagner, G.W.; Procell, L.R.; O'Connor, R.J.; Munavalli, S.; Carnes, C.L.; Kapoor, P.N.; Klabunde, K.J. Reactions of VX, GB, GD, and HD with Nanosize Al_2O_3. Formation of Aluminophosphonates. *J. Am. Chem. Soc.* **2001,** *123*, 1636–1644.

10. Bartram, P.W.; Lynn, J.T. *Decontamination Efficacy of FAST-ACT^{TM} (Phase I, Test Service Agreement Project NO. 0219T)*; ECBC-TR-277; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2003; UNCLASSIFIED Report (AD-B291 993).

11. Bartram, P.W.; Lynn, J.T. *Decomposition Kinetics of Chemical Agents on FAST-ACT^{TM} (Phase II, Test Service Agreement 0219T)*; ECBC-TR-302; U.S. Army Edgewood

Chemical Biological Center: Aberdeen Proving Ground, MD, 2003; UNCLASSIFIED Report (AD-B294 491).

12. Wagner, G.W.; Procell, L.R.; Sorrick, D.C.; Hess, Z.A.; Gehring, D.G.; Henderson, V.D.; Brickhouse, M.D.; Rastogi, V.K.; Turetsky, A.L.; Pfarr, J.W. *Development of New Decon Green®: A How-To Guide for the Rapid Decontamination of CARC Paint*; ECBC-TR-635; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2008; UNCLASSIFIED Report.

13. Yang, Y.-C.; Szafraniec, L.L.; Beaudry, W.T.; Rohrbaugh, D.K.; Procell, L.R.; Samuel, J.B. Autocatalytic Hydrolysis of V-Type Nerve Agents. *J. Org. Chem.* **1996**, *61*, 8407–8413.

14. Wagner, G.W.; Chen, Q.; Wu, Y. Reactions of VX, GD, and HD with Nanotubular Titania. *J. Phys. Chem. C* **2008**, *112*, 11901–11906.

15. Mastikhin, V.M.; Mudrakovsky, I.L.; Nosov, A.V. ^{1}H MAS Magic Angle Spinning (MAS) Studies of Heterogeneous Catalysts. *Prog. Nucl. Magn. Reson. Spectrosc.* **1991**, *23*, 259–299.

16. Mogilevsky, G.; Chen, Q.; Kulkarni, H.; Kleinhammes, A.; Mullins, W.M.; Wu, Y. Layered Nanostructures of Delaminated Anatase: Nanosheets and Nanotubes. *J. Phys. Chem. C* **2008**, *112*, 3239–3246.

APPENDIX A
REACTIVITY TEST RAW KINETIC DATA

Table A1. Kinetic Data for the Reactions of VX, GD, and HD with Candidate Sorbents.

Sorbent	VX				GD				HD			
	Fresh		Air-Exposed		Fresh		Air-Exposed		Fresh		Air-Exposed	
	time, h	amount	time	amount	time, h	amount	time, h	amount	time, h	amount	time, h	amount
nMgO #1	0.18	63	0.16	93.6	0.18	46	0.16	66	0.14	169	0.14	168
	0.36	47	0.31	92.4	0.33	25	0.33	57	0.33	168	0.44	162
	0.59	39	0.71	89.5	0.73	8.6	0.71	42	0.69	163	0.74	160
	0.83	36	1.11	87.2	1.13	4.0	1.11	26	1.01	166	1.01	158
	1.14	36	3.26	80.2	1.53	1.0	1.76	12	2.16	151	2.86	139
	1.91	31	5.41	74.4			2.41	2.7	3.30	143	4.66	135
	2.28	27	7.56	70.9			3.06	1.0	4.59	132	6.83	123
	3.43	21	9.71	68.0					6.74	113	8.96	111
	4.58	16	11.86	66.3					8.89	103	11.11	109
	6.73	11	14.01	62.8					11.04	92	13.26	100
	8.88	8.7	16.16	61.0					13.21	88	15.41	94
	11.03	6.7	18.31	59.9					15.34	78	17.56	94
	13.18	4.7	20.46	57.0					17.49	69	19.71	91
	15.33	3.3	22.61	56.0					19.64	70	21.86	87
	17.48	2.7	24.01	55.0					21.79	65	24.01	84
	19.64	2.0							23.94	56		
	20.84	1.7										
	21.88	1.0										
nMgO #2	0.23	67.3	0.21	94.1	0.18	46.0	0.14	70.6	0.16	156	0.14	150
	0.38	62.4	0.36	89.4	0.33	25.0	0.29	60	0.53	150	0.31	149
	0.61	55.6	0.76	91.8	0.73	8.6	0.69	51	0.76	144	0.63	148
	0.84	47.9	1.16	90.0	1.13	4.0	1.09	37	1.13	138	1.03	145
	1.08	46.0	3.31	85.3	1.53	1.0	1.74	27	1.78	127	1.68	142
	1.41	45.0	5.46	85.9			2.39	15	2.42	125	2.83	132
	2.13	42.0	7.61	80.0			3.04	7.1	3.08	119	4.98	130
	3.28	33.3	9.76	78.8			3.69	2.9	3.73	110	7.13	119

Table A1. Kinetic Data for the Reactions of VX, GD, and HD with Candidate Sorbents. (Continued)

	4.43	31.0	11.91	77.1			4.71	1.2	5.14	108	9.28	115
	5.58	26.0	14.06	74.7					7.13	101	11.43	109
	6.73	21.0	16.21	74.7					9.44	83	13.58	111
	8.88	21.0	18.36	74.1					11.59	78	15.74	105
	12.03	18.0	20.51	71.8					13.74	73	17.88	107
	14.18	16.0	22.66	70.0					15.89	68	20.41	100
	16.33	13.0	24.01	66.5					18.08	57	24.94	90
	19.23	13.0							22.34	57		
	21.44	12.0							25.01	48		
	24.01	9.6										
nMgO #3	not	done	not	done	not	done	not	done	0	100	not	done
									0.18	86.2		
									0.33	81.8		
									0.56	76.7		
									0.79	75.5		
									1.11	72.3		
									1.76	67.3		
									2.41	64.8		
									3.06	61.0		
									3.71	59.7		
									5.09	55.3		
									7.24	51.6		
									9.39	46.5		
									11.54	45.3		
									13.69	40.9		
									15.84	39.0		
									18.01	37.7		
									20.14	34.0		
									22.29	31.4		
									24.11	32.7		
$nTiO_2$ #1	Run 1	Run 1	Run 1	Run 1	0.21	21	0.16	44	0.19	143	0.16	163

Table A1. Kinetic Data for the Reactions of VX, GD, and HD with Candidate Sorbents. (Continued)

	0.19	24.2	0	100	0.36	18	0.33	30	0.38	125	0.33	133
	0.34	13.1	11.5	0.83	0.68	14	0.71	16	0.56	115	0.58	116
	0.49	10.0	(min)		1.01	14	1.11	7.9	0.74	103	0.98	104
	0.64	4.8			1.38	8.6	1.49	6.1	1.01	98	1.44	86
	0.79	4.8			2.02	7.9	1.89	6.1	1.29	93	2.59	78
	1.26	3.8			2.68	6.4	2.29	1.4	1.64	84	3.74	69
	1.49	1.9			3.33	5.0	2.69	1.0	2.29	80	4.91	62
	1.73	1.3			3.98	4.5			3.44	69	7.06	48
	1.96	0.60			4.63	4.1			5.04	57	9.21	45
					5.41	3.8			7.08	48	11.36	40
	Run 2	Run 2	Run 2	Run 2	6.56	2.4			9.23	40	13.51	43
	0.18	46.8	0	100	7.83	2.0			11.38	38	15.66	33
	0.33	34.0	17.5	1.0	9.99	1.6			13.53	36	17.81	31
	0.48	23.0	(min)		12.13	1.0			15.53	35	19.96	24
	0.63	17.0							17.83	28	22.11	23
	0.78	15.0							19.98	27	24.04	17
	1.01	8.4							22.13	23		
	1.33	4.8							24.08	25		
	1.64	2.6										
	1.96	2.0										
	2.28	1.0										
$nTiO_2$ #2	0	100	11.5	31.7	0	100	0.19	67.6	0	100	0	100
	0.23	91.4	20.5	14.2	0.19	65.7	0.34	34.5	0.19	95.1	0.19	90.8
	0.38	69.8	29.5	8.2	0.34	42.9	0.58	14.5	0.34	81.1	0.34	84.9
	0.53	58.0	38.5	3.3	0.58	34.3	0.81	9.7	0.58	74.4	0.74	70.4
	0.68	50.6	47.5	1.6	0.81	28.6	1.04	6.9	0.81	70.1	0.98	60.5
	0.84	42.6	56.5	0.82	1.04	26.9	1.44	2.8	1.04	70.1	1.21	57.9
	0.98	34.0	(min)		1.44	26.9	2.09	1.0	1.46	62.8	1.61	57.2
	1.21	27.8			2.09	13.7			2.16	60.4	2.26	50.0
	1.46	23.5			2.74	9.1			2.76	57.9	2.91	47.4

Table A1. Kinetic Data for the Reactions of VX, GD, and HD with Candidate Sorbents. (Continued)

	1.68	14.2			3.39	6.9			3.46	59.1	3.56	40.8
	1.91	11.1			4.04	5.1			4.56	56.7	4.23	36.8
	2.14	9.3			4.69	3.4			5.71	54.9	4.83	35.5
	2.38	6.2			5.84	1.7			7.86	52.4	6.98	30.3
	2.61	6.8							10.01	47.6	9.13	28.3
	2.84	3.7							12.16	48.2	11.28	25.0
	3.08	4.3							14.31	46.3	13.43	25.7
	3.31	2.5							16.46	40.2	15.58	20.4
	3.54	1.9							18.61	37.8	17.73	16.4
	3.78	1.2							20.76	38.4	19.88	11.8
	4.01	1.0							22.91	38.4	22.03	12.5
									24.06	38.4	24.14	9.2
nAl_2O_3	0.19	81.6	0.24	90.8	0.23	60	0.18	57	0.16	121	0.16	140
	0.34	76.1	0.39	89.1	0.38	57	0.33	48	0.34	114	0.36	124
	0.58	69.9	0.63	81.6	0.66	53	0.64	40	0.68	109	0.67	102
	0.81	66.3	1.03	75.3	1.01	48	1.01	34	1.11	102	1.01	89
	1.04	62.0	1.69	67.2	1.41	44	2.01	24	1.54	92	1.84	78
	1.44	61.3	2.83	60.3	1.91	36	3.24	14	2.69	82	2.49	70
	2.09	58.0	4.98	50.0	2.66	34	5.39	8.8	3.84	82	3.14	65
	3.24	54.0	7.13	45.0	3.81	28	7.54	4.4	4.99	67	3.79	56
	5.39	48.0	9.28	40.0	4.96	21	9.69	1.8	6.83	62	4.66	51
	7.54	45.0	11.43	36.0	6.44	16	11.83	0.74	8.98	62	6.81	42
	9.69	42.0	13.58	32.0	8.59	8.8	13.99	0	11.13	60	8.96	32
	11.84	38.0	15.73	30.0	10.74	5.5			13.28	52	11.11	30
	13.99	38.0	17.88	28.0	12.89	3.6			15.43	50	13.26	27
	16.14	36.0	20.03	27.0	15.04	1.8			17.58	52	15.41	19
	19.06	35.0	22.18	24.0	17.19	1.1			19.73	44	17.56	11
	21.59	32.0	24.33	24.0	19.34	1.1			21.88	48	19.71	12
	24.04	32.0	64.86	9.8	21.49	0.36			24.03	47	21.86	9
					24.49	0					24.13	4
FAST-ACT	0.23	100	0.19	98.8	0.21	29.2	0.18	67.5	0	100	0	100

Table A1. Kinetic Data for the Reactions of VX, GD, and HD with Candidate Sorbents. (Continued)

	0.38	86.0	0.34	77.8	0.38	17.5	0.33	55.0	0.23	76.2	0.18	93.7
	0.53	76.2	0.49	67.7	0.59	10.0	0.56	38.8	0.39	67.8	0.33	81.0
	0.68	70.7	0.64	61.1	0.83	7.3	0.79	30.0	0.78	69.6	0.56	79.7
	0.83	65.8	0.79	53.9	1.06	3.2	1.03	22.5	1.01	62.6	0.79	77.2
	0.98	63.4	0.94	51.5	1.46	1.1	1.26	18.1	1.51	59.8	1.03	73.4
	1.63	48.8	1.66	37.7					2.01	53.7	1.43	69.0
	2.28	38.4	2.31	41.3					3.16	48.6	2.08	63.3
	2.93	26.2	2.96	29.9					4.31	50.0	2.73	56.3
	3.58	25.6	3.61	22.8					5.46	48.1	3.38	50.6
	4.23	17.1	4.26	22.8					6.61	47.2	4.03	48.1
	4.88	18.3	4.91	19.2					8.76	49.1	4.68	41.8
	6.03	12.2	6.78	14.4					10.91	41.6	6.83	38.0
	7.18	11.0	8.93	9.0					13.06	40.2	8.98	36.1
	8.33	6.10	11.08	7.2					15.38	37.9	11.13	31.6
	9.48	4.3	13.23	4.2					17.53	39.7	13.28	31.0
	11.63	1.8	15.38	3.6					19.68	39.3	15.43	27.8
	13.78	1.0	17.53	2.4					21.83	34.1	17.58	20.9
			19.68	1.8					24.04	34.6	19.73	18.4
											21.88	20.3
											24.03	15.8
FAST-ACT 2	0.21	100	0	100	0.19	53.8	0	100	0	100	0	100
	0.36	88.2	0.34	89.6	0.34	45.6	0.19	67.6	0.19	93.7	0.19	98.3
	0.51	80.9	0.49	81.6	0.58	35.0	0.34	46.8	0.36	89.9	0.34	90.2
	0.66	70.6	0.73	68.0	0.81	30.0	0.58	35.8	0.54	82.9	0.58	86.7
	0.81	63.2	0.96	70.4	1.04	23.8	0.81	22.0	1.09	75.9	0.81	76.9
	0.96	66.2	1.19	68.0	1.28	23.8	1.04	15.0	1.74	69.6	1.04	74.0
	1.61	51.5	1.41	60.8	1.51	27.5	1.28	8.1	2.39	69.0	1.44	72.8
	2.26	47.8	2.19	39.2	1.71	14.4	1.51	8.7	3.54	63.3	2.09	67.6
	2.91	35.3	3.34	22.4	1.94	17.5	1.74	4.6	4.69	60.8	2.74	66.5
	3.56	36.8	5.49	8.0	2.18	15.6	1.98	3.5	5.84	54.4	3.39	60.1
	5.88	25.7			2.41	15.6	2.21	1.7	8.44	46.8	4.04	57.2

Table A1. Kinetic Data for the Reactions of VX, GD, and HD with Candidate Sorbents. (Continued)

	7.04	13.2			2.88	10.0			10.59	44.3	4.69	54.3
	9.18	8.1			2.98	8.8			12.74	44.3	6.84	47.4
	11.33	5.9			3.36	8.1			14.89	37.3	8.99	43.9
	13.48	5.1			3.83	4.4			17.04	34.8	11.14	37.6
	15.63	2.9			4.28	4.4			19.19	33.5	13.29	32.4
	17.78	1.5							21.34	32.3	15.43	31.2
	20.93	1.0							23.49	31.0	17.59	30.1
									24.14	28.5	19.74	24.9
											21.89	21.4
											23.04	20.8
A-200	0.18	88.1	0.18	79.5	0.23	49	0.14	57	0.16	163	0.21	163
	0.33	87.4	0.33	78.3	0.38	37	0.29	52	0.34	156	0.36	160
	0.56	84.6	0.56	75.2	0.53	33	0.61	43	0.68	151	0.63	154
	0.89	81.8	0.88	74.5	0.69	29	1.01	38	1.09	147	1.01	150
	1.19	82.5	1.19	73.9	1.01	21	1.59	32	2.09	147	2.19	137
	2.41	71.3	3.34	66.5	2.23	18	2.41	28	21.49	96	3.34	128
	4.56	69.0	5.49	59.6	2.43	17	3.06	25	24.03	85	4.49	121
	6.71	66.0	7.64	59.0	2.83	12	3.81	20			5.09	111
	8.86	62.0	9.79	55.2	3.23	9.7	5.96	13			7.24	107
	11.01	57.0	11.94	54.0	3.63	11	8.11	11			9.39	98
	13.16	57.0	14.09	52.2	4.03	7.9	10.26	6.6			11.54	90
	15.31	55.0	16.24	49.7	5.36	5.2	12.41	6.0			13.31	87
	17.46	51.0	18.39	49.7	6.49	2.4	14.56	4.3			15.84	85
	19.61	51.0	20.54	49.1	8.64	2.8	16.71	2.3			17.99	76
	22.36	48.0	22.69	49.1	10.79	3.4	18.86	3.0			20.14	73
	24.01	51.0	24.09	46.0	12.94	1.7	21.01	0.99			22.29	70
					15.09	2.1	23.16	1.3			24.14	69
					17.24	1.4	24.31	0.33				
					19.39	1.0						
					21.54	1.4						
					24.04	2.1						

Blank

APPENDIX B
REACTIVITY TEST SELECT MAS NMR SPECTRA

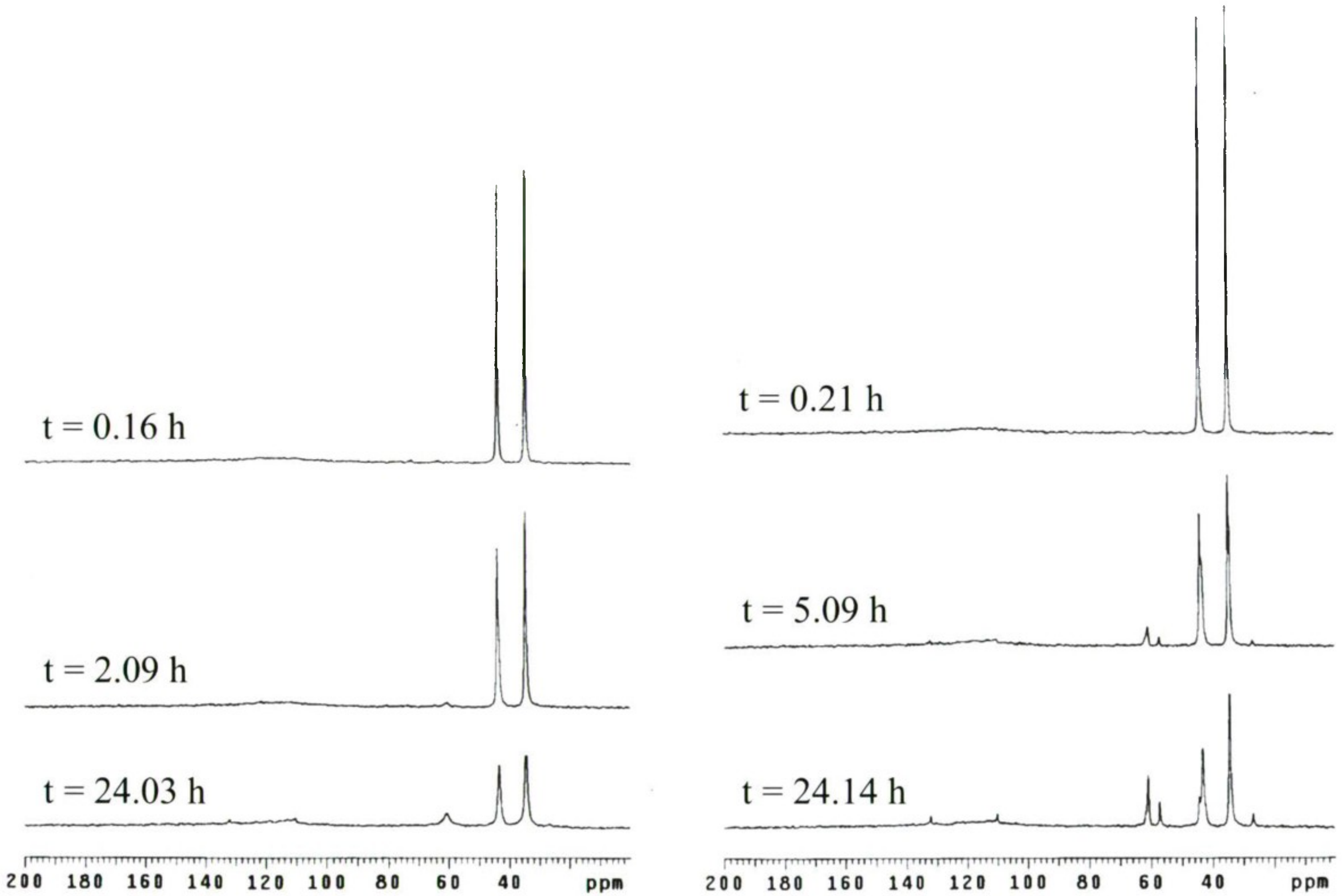

Figure B1. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.0833 g fresh (left) and 0.0873 g air-exposed (right) A-200 at the indicated reaction times.

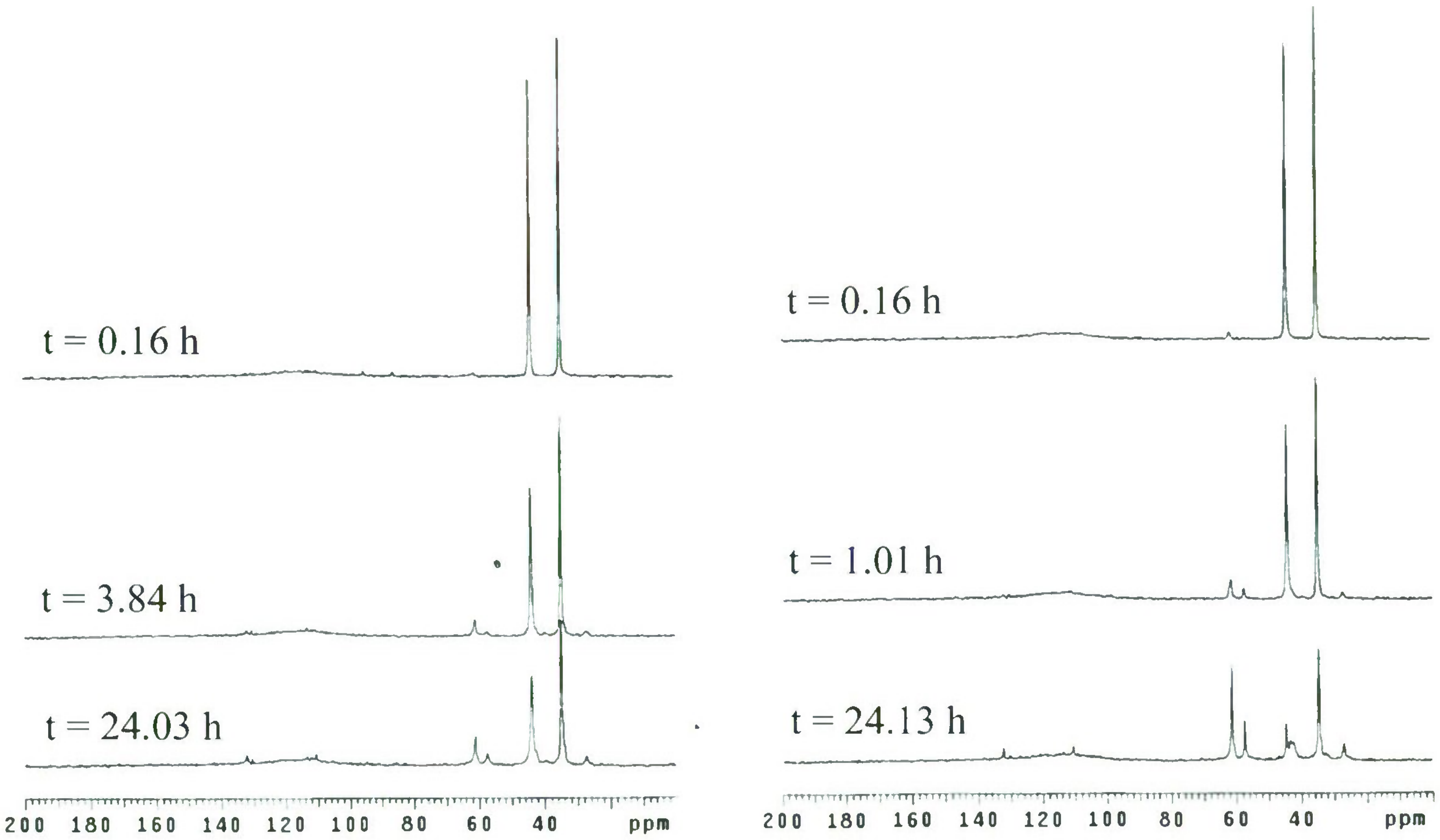

Figure B2. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.0999 g fresh (left) and 0.0979 g air-exposed (right) nAl_2O_3 at the indicated reaction times.

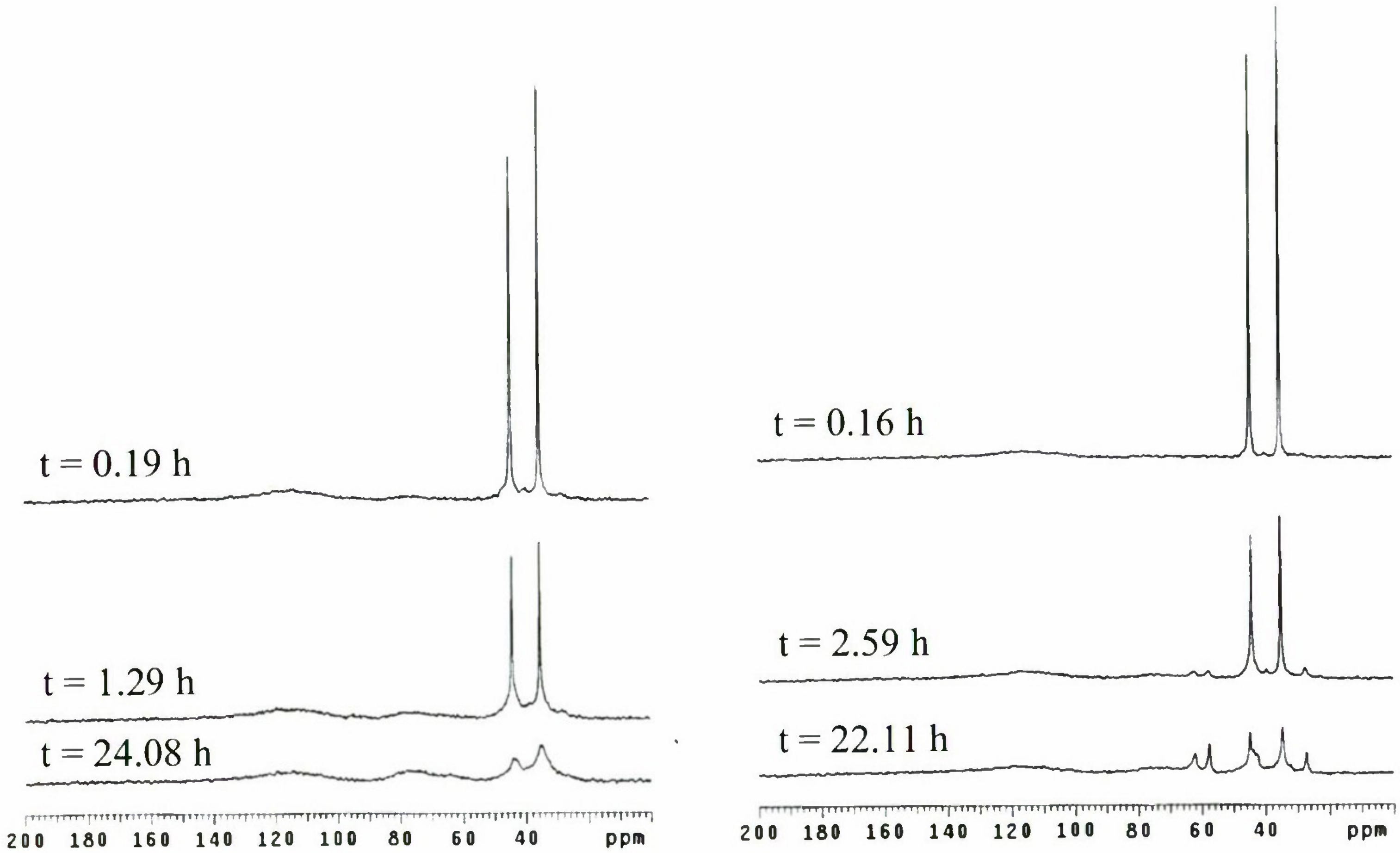

Figure B3. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.1776 g fresh (left) and 0.2226 g air-exposed (right) $nTiO_2$ #1 at the indicated reaction times.

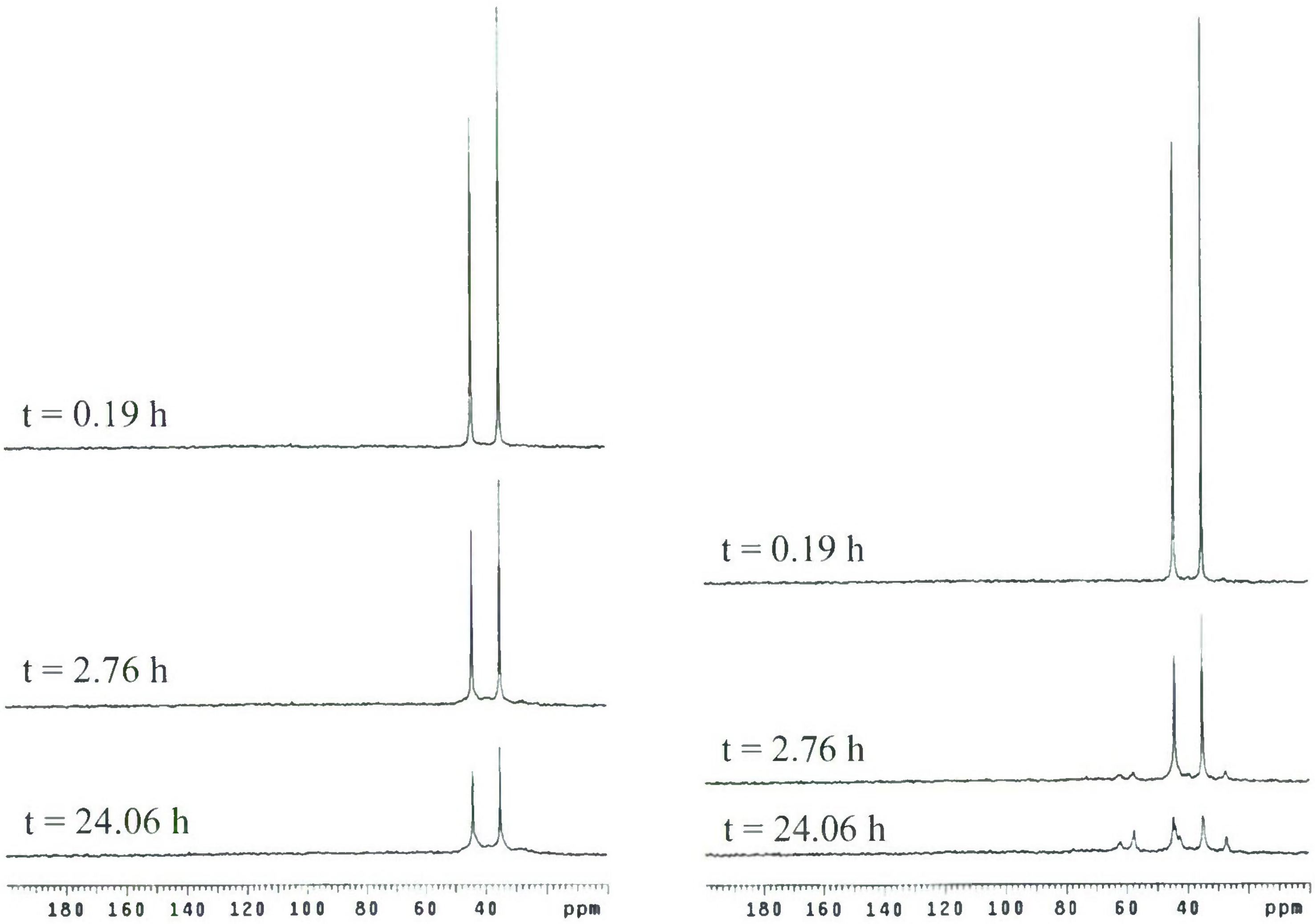

Figure B4. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.1126 g fresh (left) and 0.1209 g air-exposed (right) $nTiO_2$ #2 at the indicated reaction times.

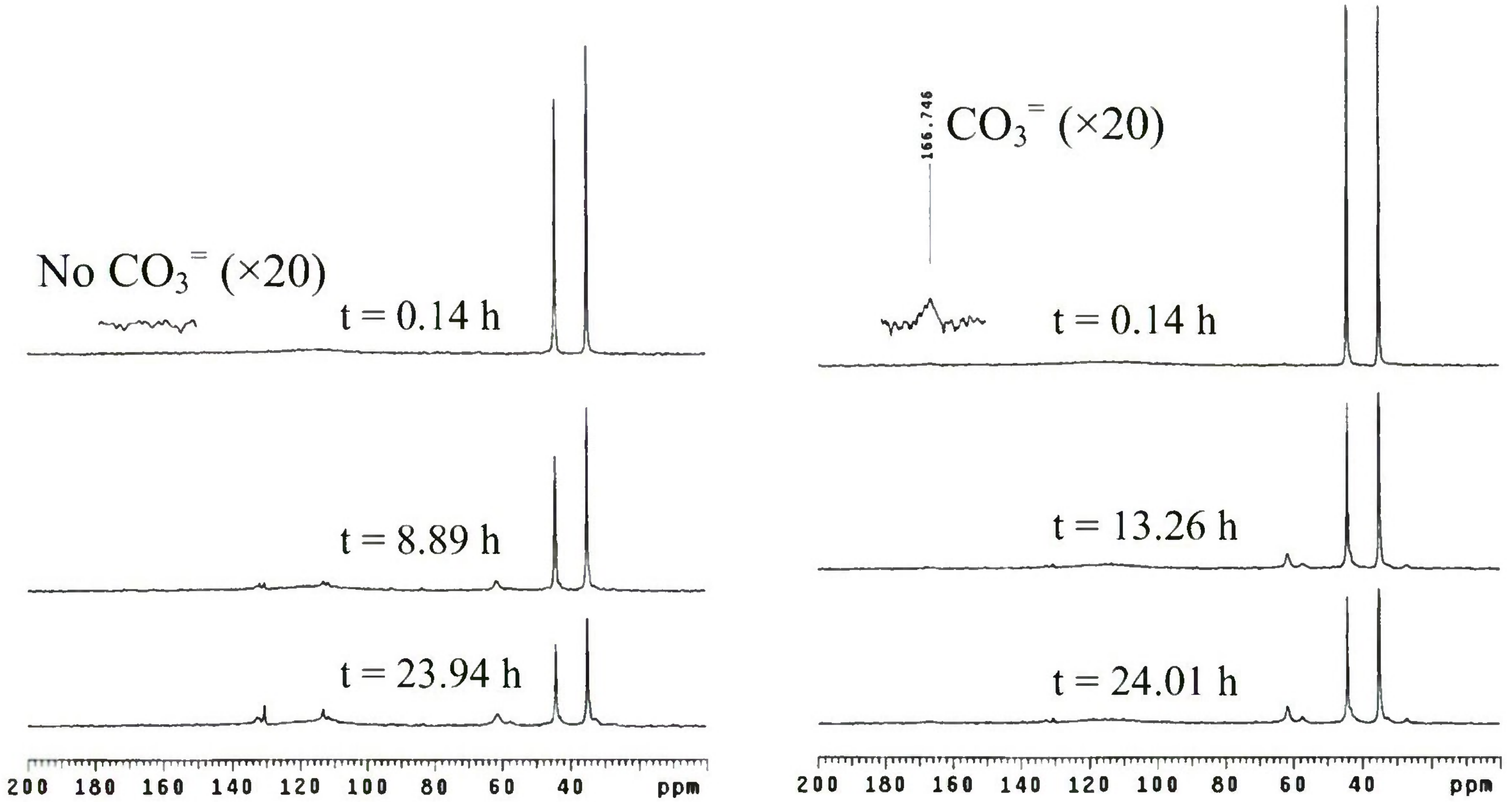

Figure B5. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.1320 g fresh (left) and 0.1866 g air-exposed (right) nMgO #1 at the indicated reaction times. Insets show enhanced regions (×20 zoom) for the carbonate ($CO_3^{=}$) peak vicinity (ca. 167 ppm) which was only detected in the air-exposed sample

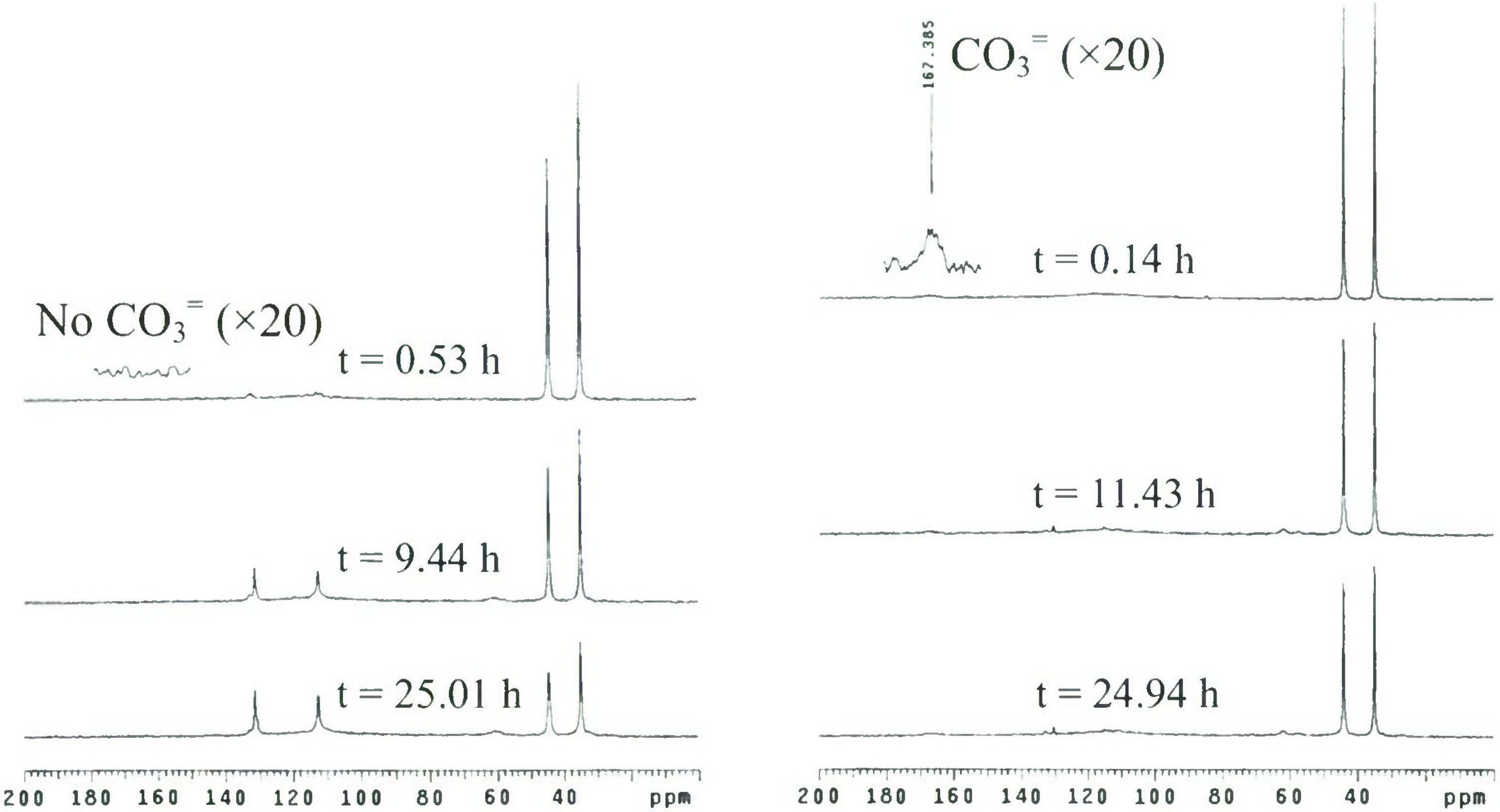

Figure B6. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.1930 g fresh (left) and 0.2334 g air-exposed (right) nMgO #2 at the indicated reaction times. Insets show enhanced regions (×20 zoom) for the carbonate ($CO_3^=$) peak vicinity (ca. 167 ppm) which was only detected in the air-exposed sample

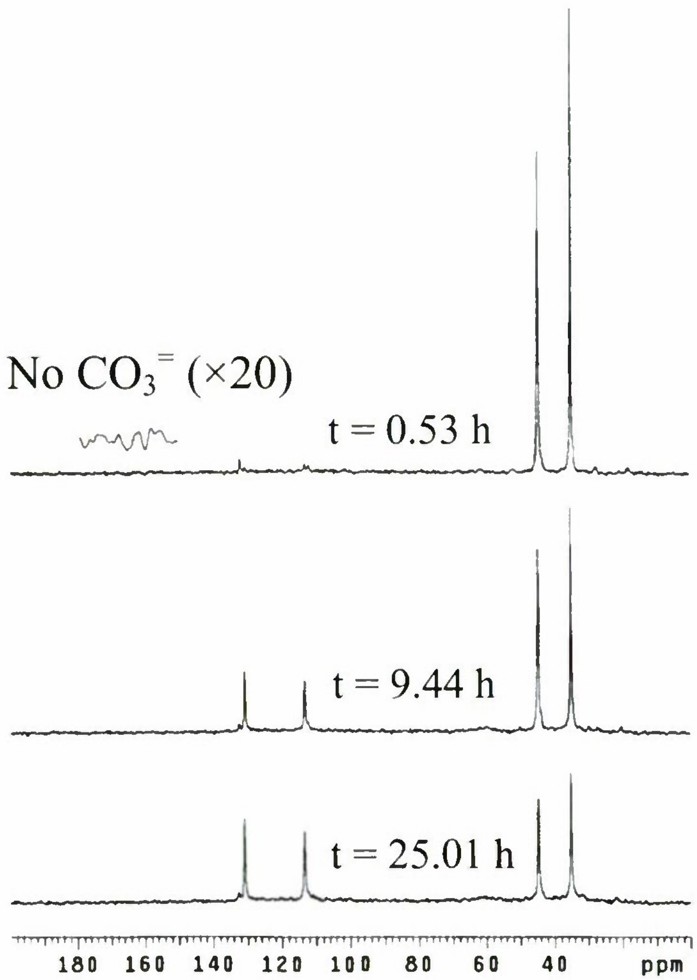

Figure B7. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.1319 g fresh nMgO #3 at the indicated reaction times. Inset shows the carbonate ($CO_3^{=}$) peak region (×20 zoom) where none was detected.

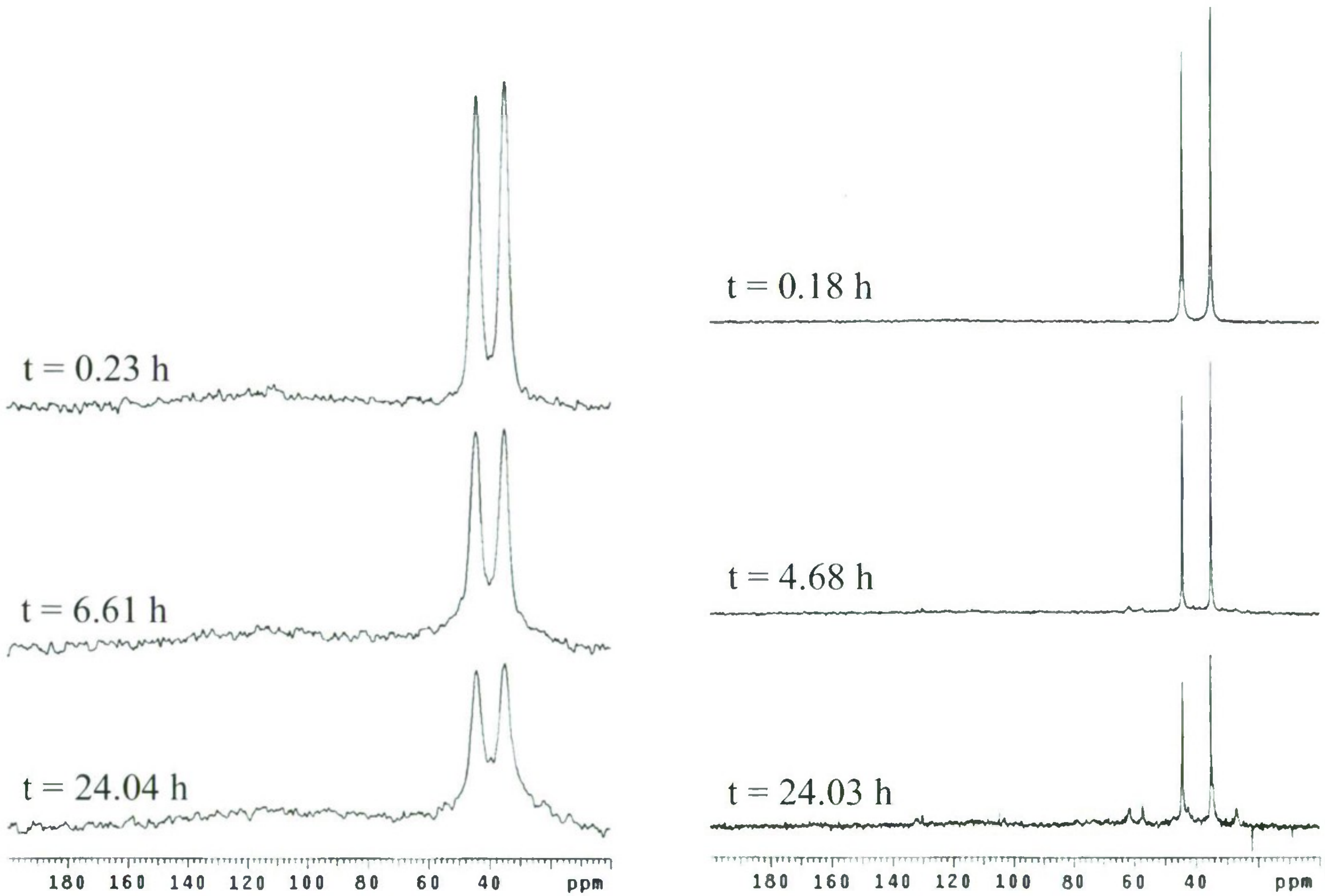

Figure B8. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.2020 g fresh (left) and 0.2244 g air-exposed (right) FAST-ACT at the indicated reaction times.

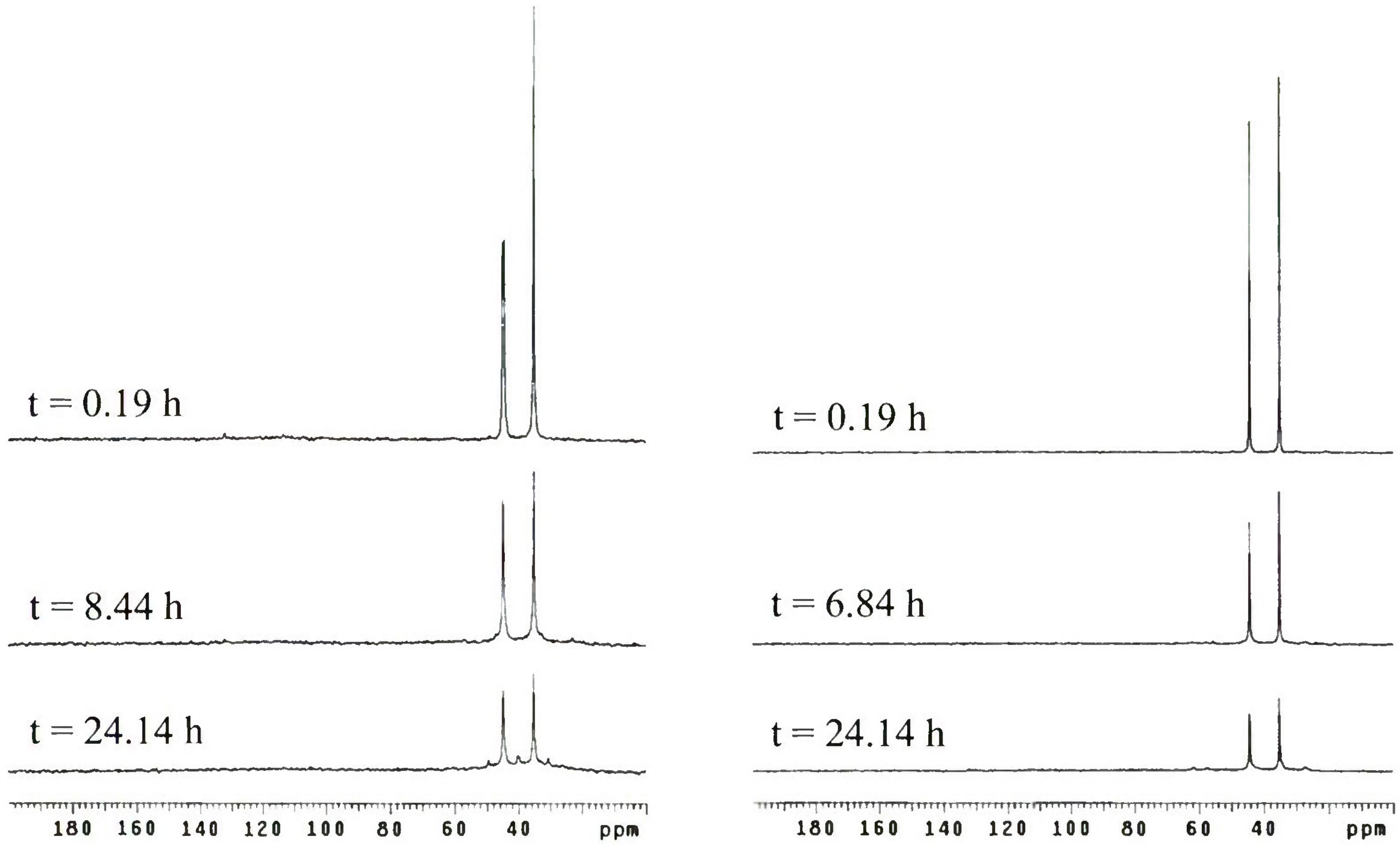

Figure B9. Select ^{13}C MAS NMR spectra obtained for 5 μL HD* added to 0.1194 g fresh (left) and 0.1357 g air-exposed (right) FAST-ACT 2 at the indicated reaction times.

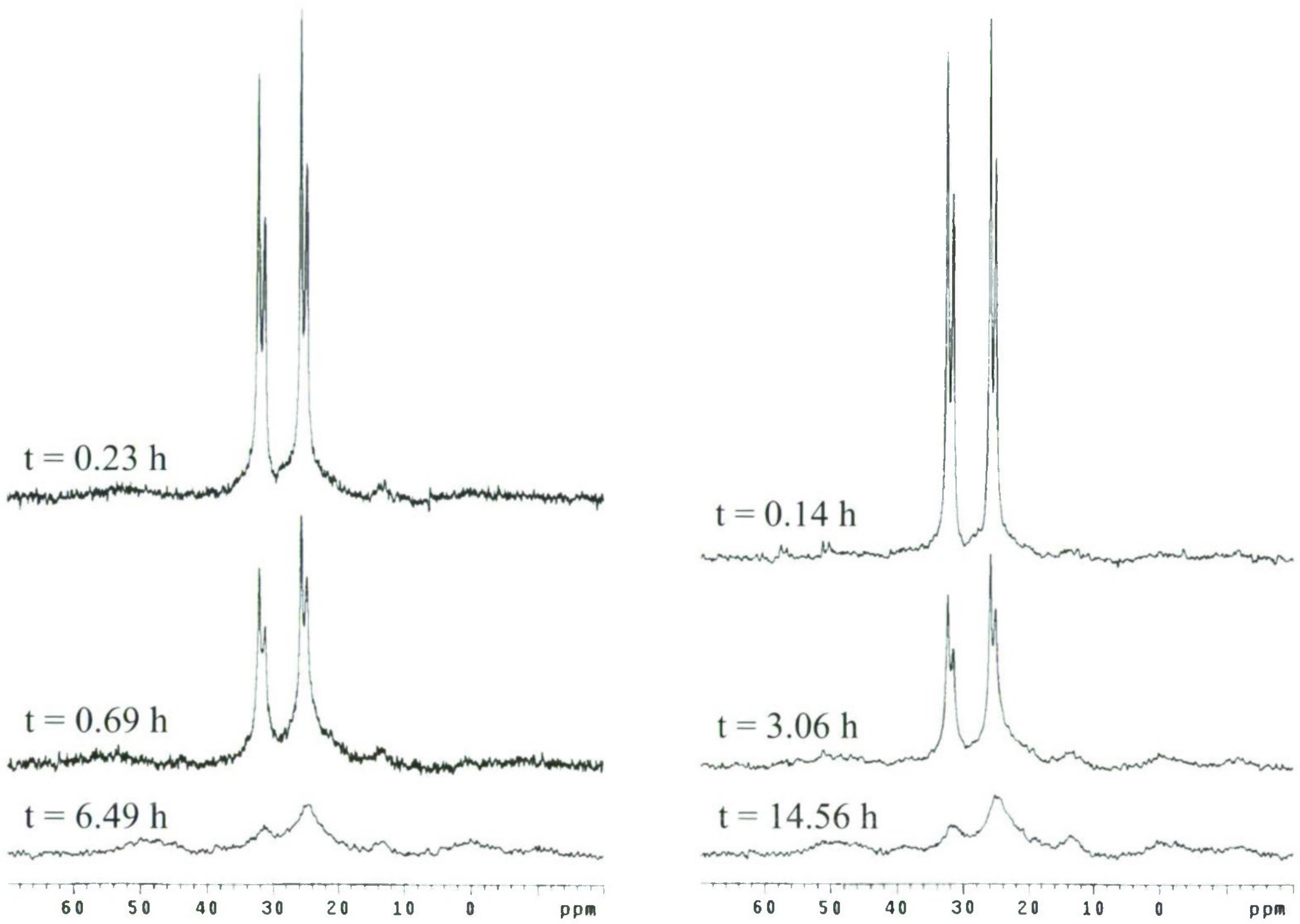

Figure B10. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.0885 g fresh (left) and 0.0928 g air-exposed (right) A-200 at the indicated reaction times.

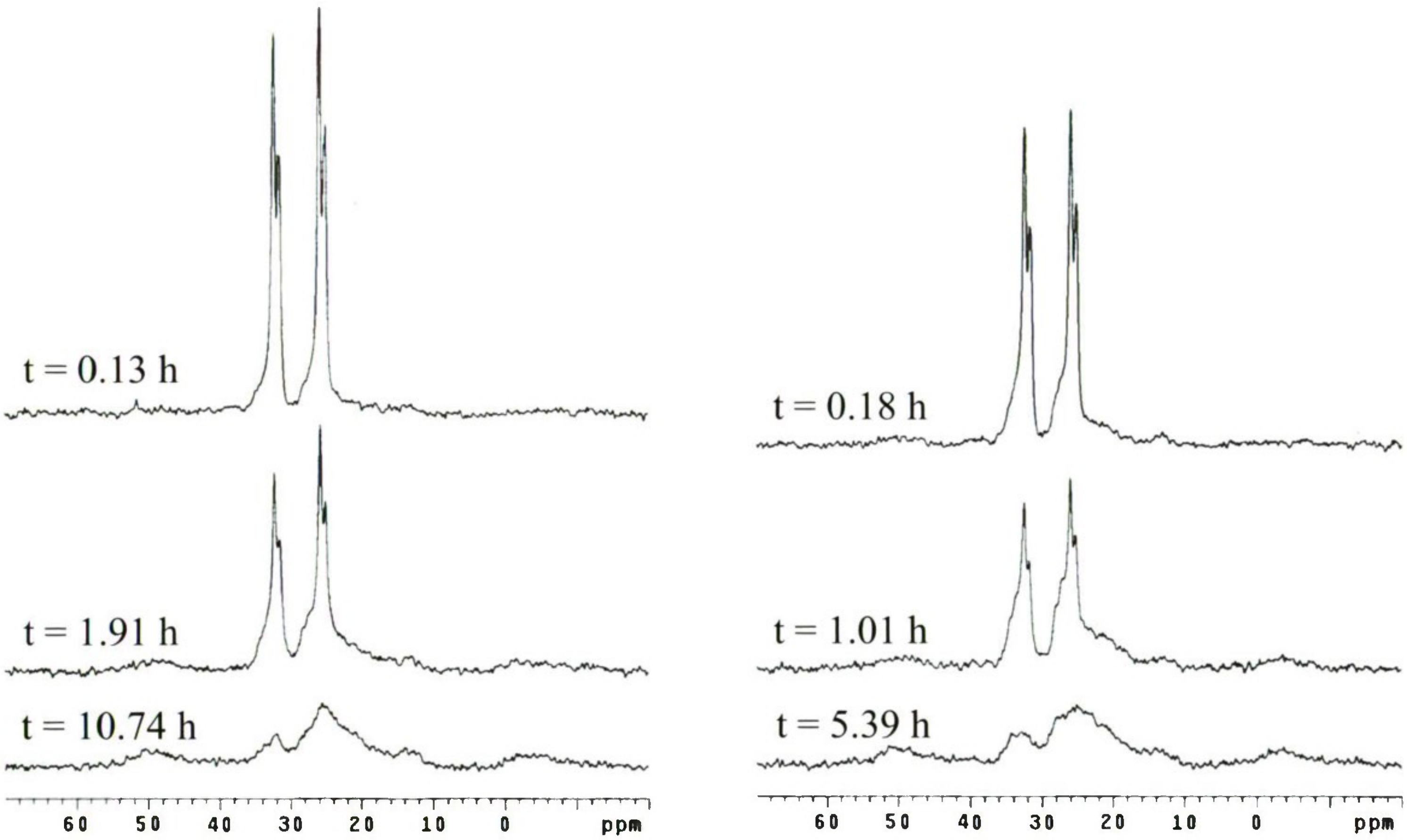

Figure B11. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.1031 g fresh (left) and 0.1073 g air-exposed (right) nAl_2O_3 at the indicated reaction times.

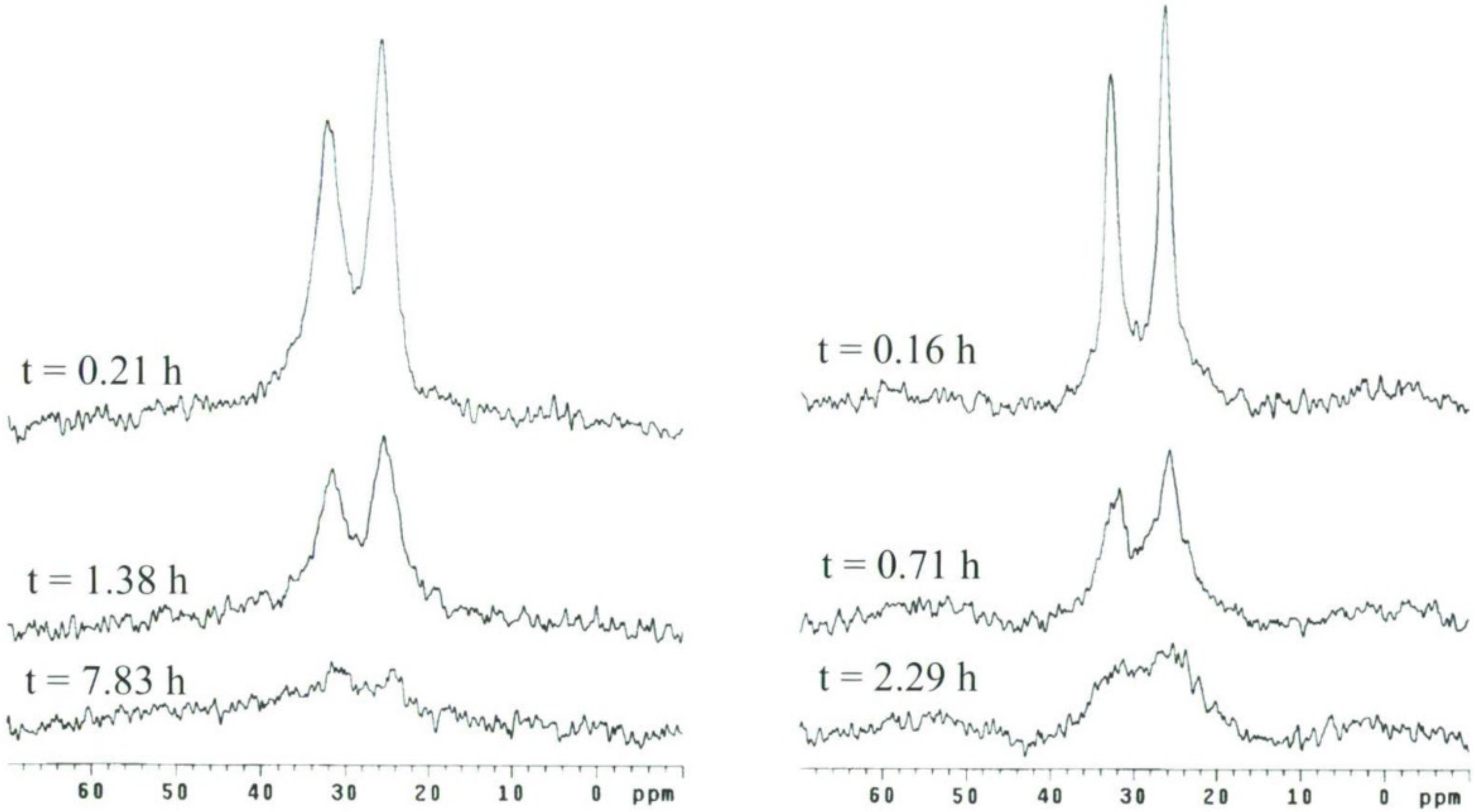

Figure B12. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.2077 g fresh (left) and 0.2470 g air-exposed (right) $nTiO_2$ at the indicated reaction times.

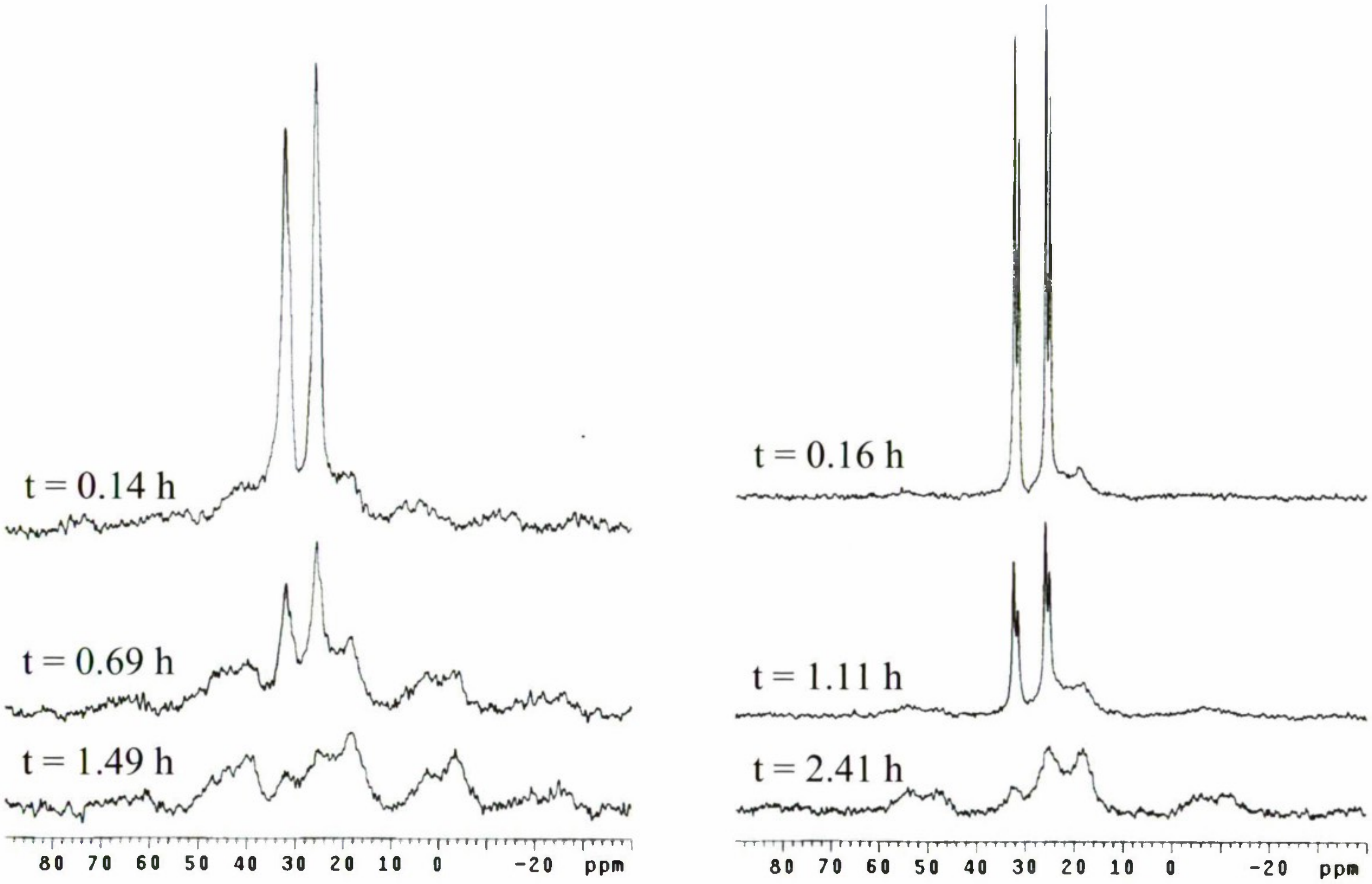

Figure B13. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.1428 g fresh (left) and 0.1915 g air-exposed (right) nMgO #1 at the indicated reaction times.

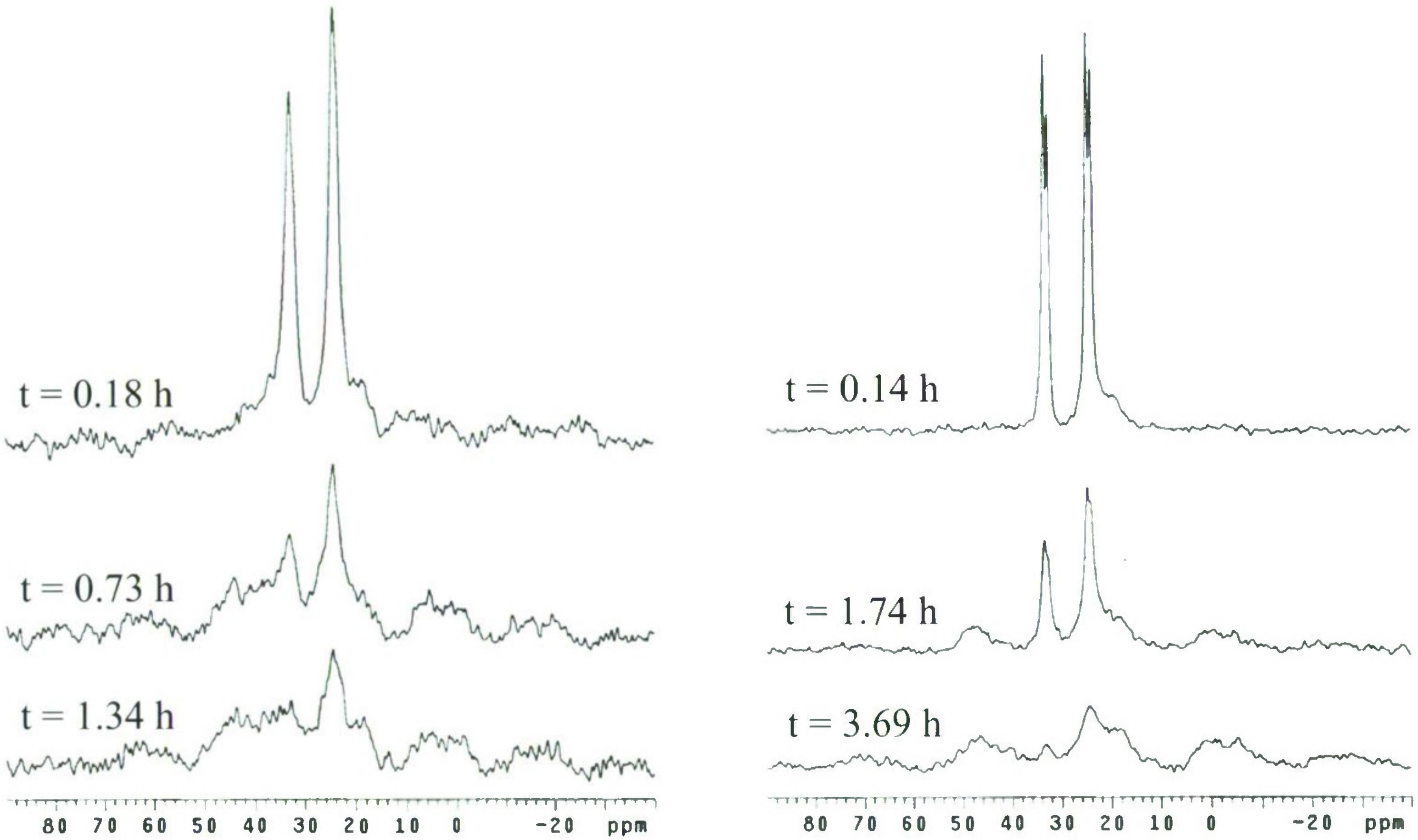

Figure B14. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.1858 g fresh (left) and 0.2518 g air-exposed (right) nMgO #2 at the indicated reaction times.

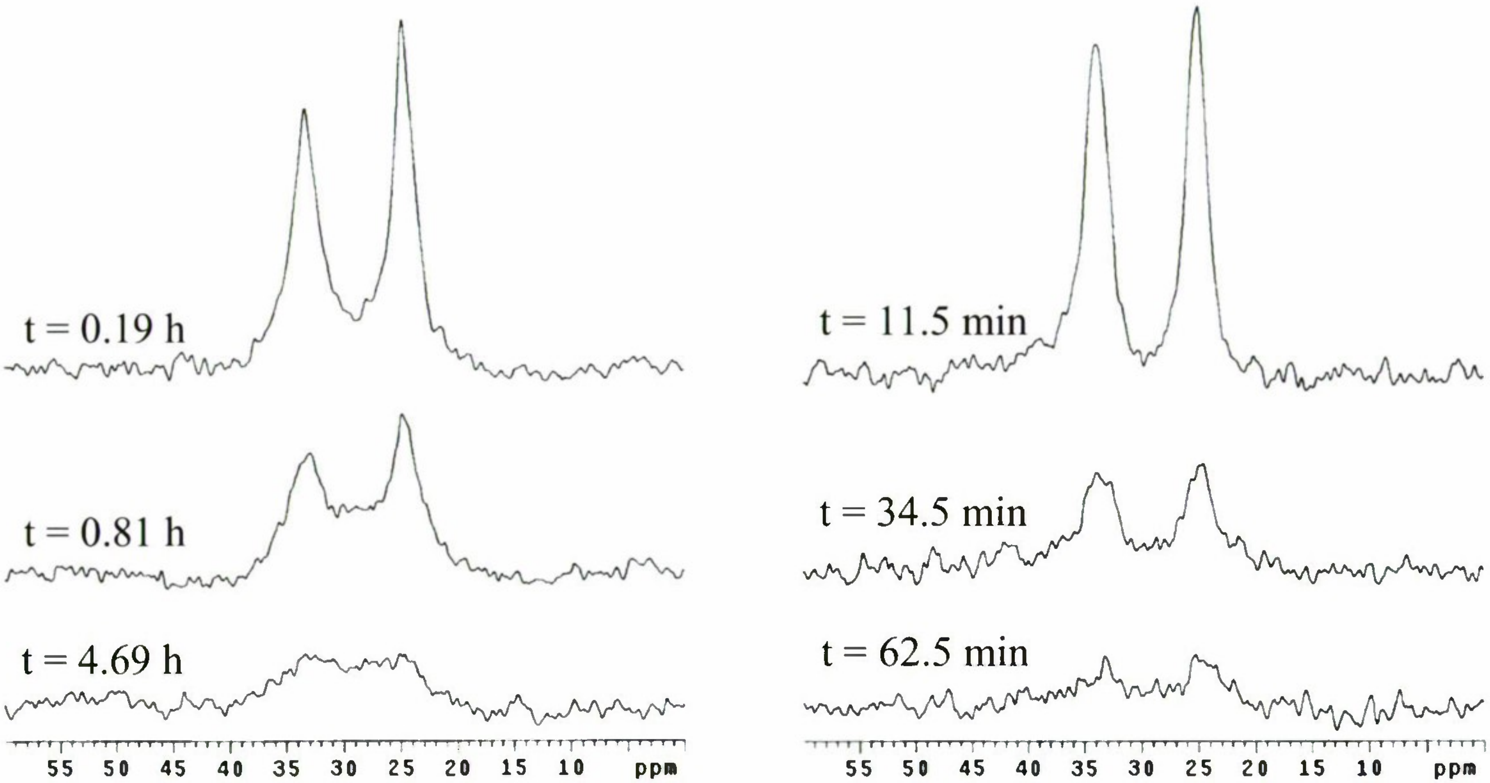

Figure B15. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.1137 g fresh (left) and 0.1444 g air-exposed (right) $nTiO_2$ #2 at the indicated reaction times.

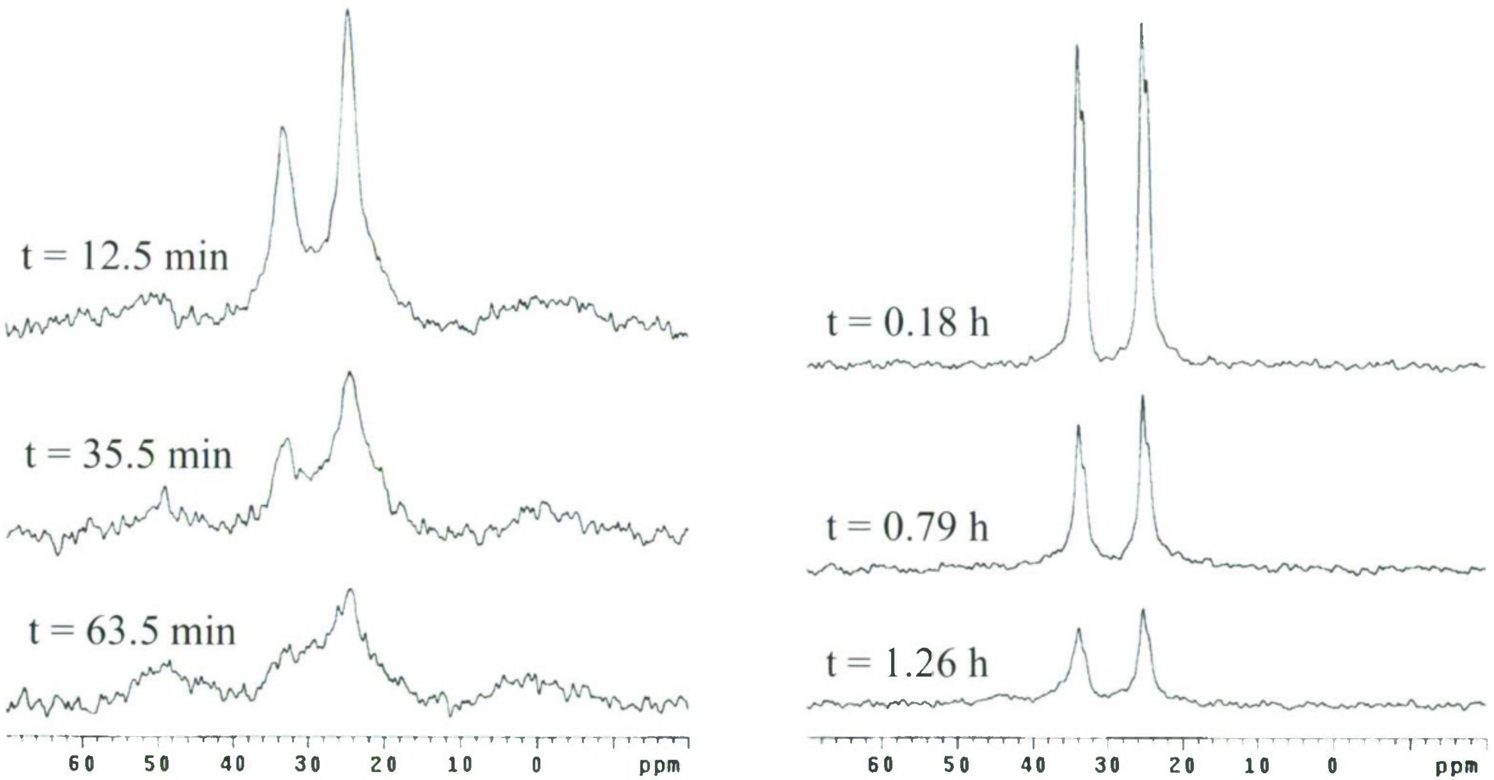

Figure B16. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.1761 g fresh (left) and 0.2376 g air-exposed (right) FAST-ACT at the indicated reaction times.

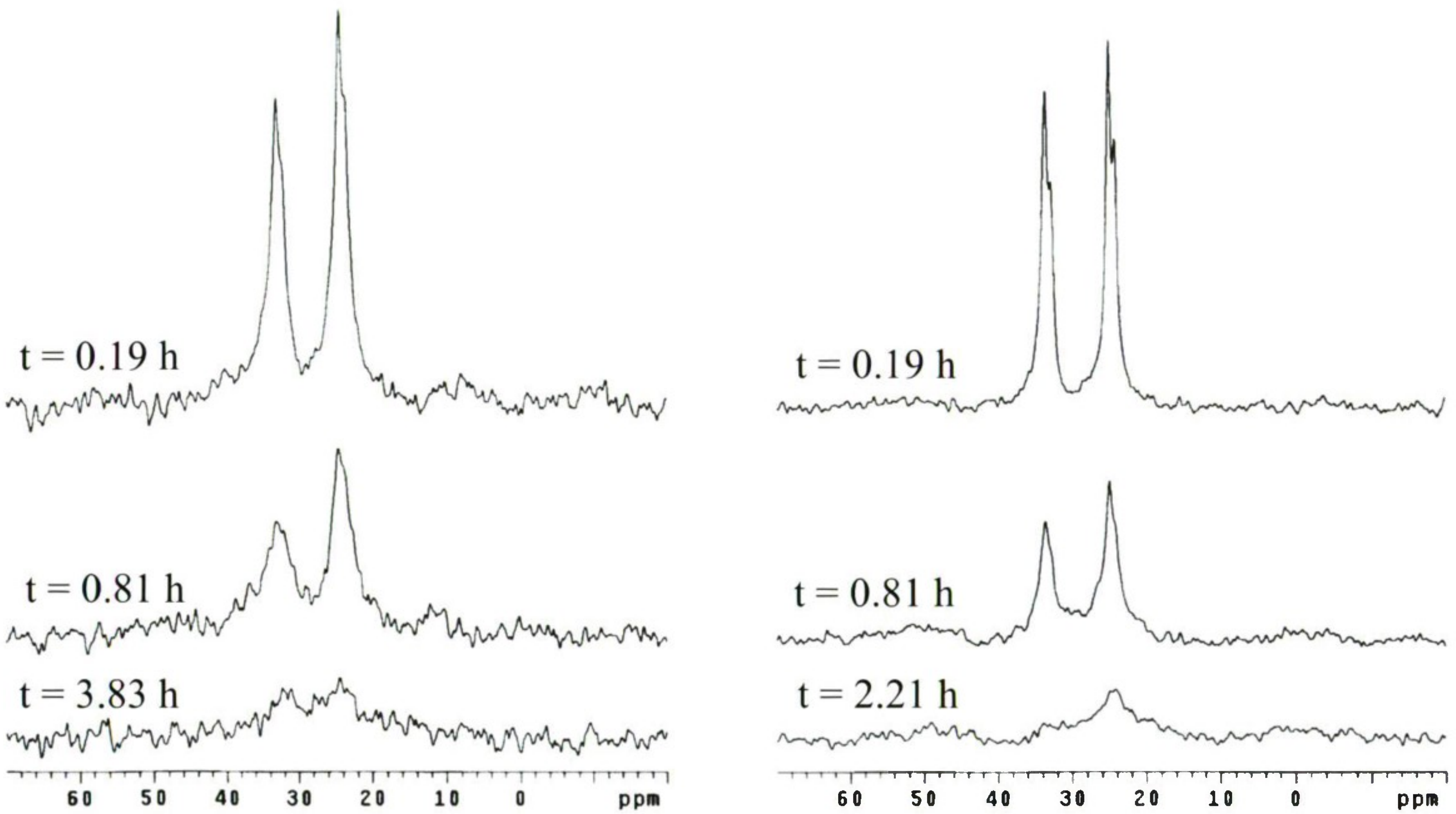

Figure B17. Select ^{31}P MAS NMR spectra obtained for 5 μL GD added to 0.1250 g fresh (left) and 0.1563 g air-exposed (right) FAST-ACT 2 at the indicated reaction times.

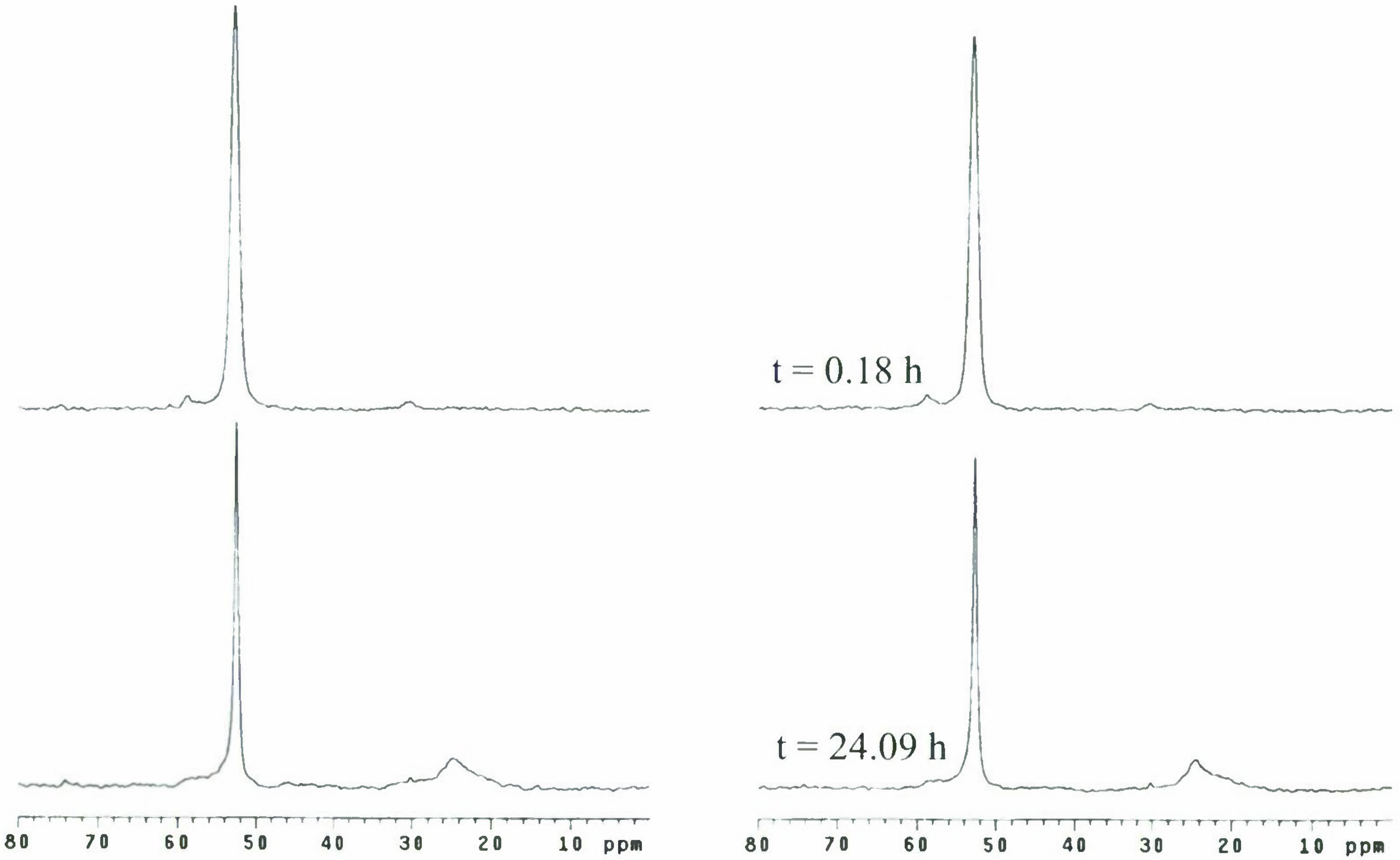

Figure B18. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.0983 g fresh (left) and 0.0931 g air-exposed (right) A-200 at the indicated reaction times.

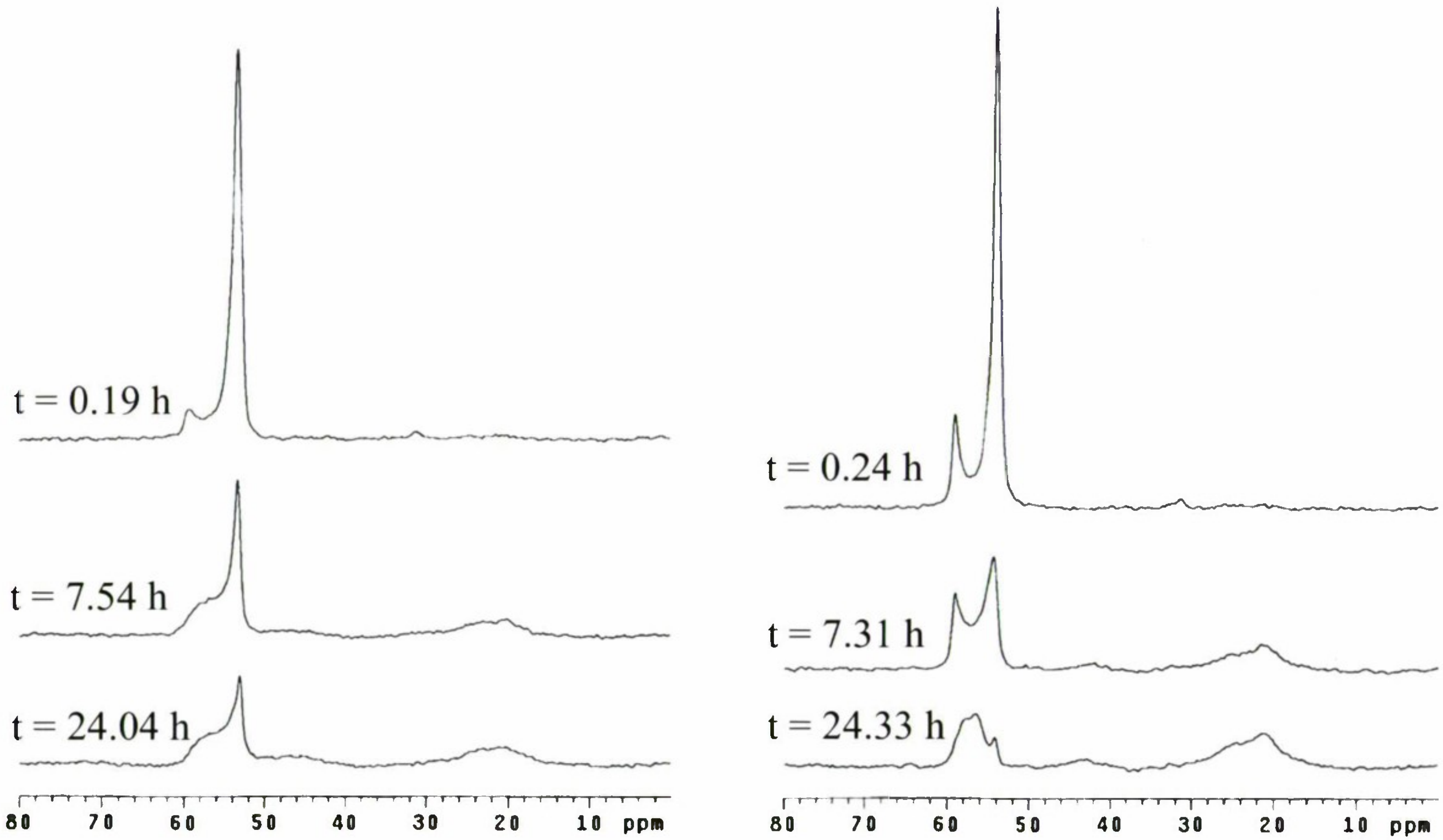

Figure B19. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.0931 g fresh (left) and 0.1031 g air-exposed (right) nAl_2O_3 at the indicated reaction times.

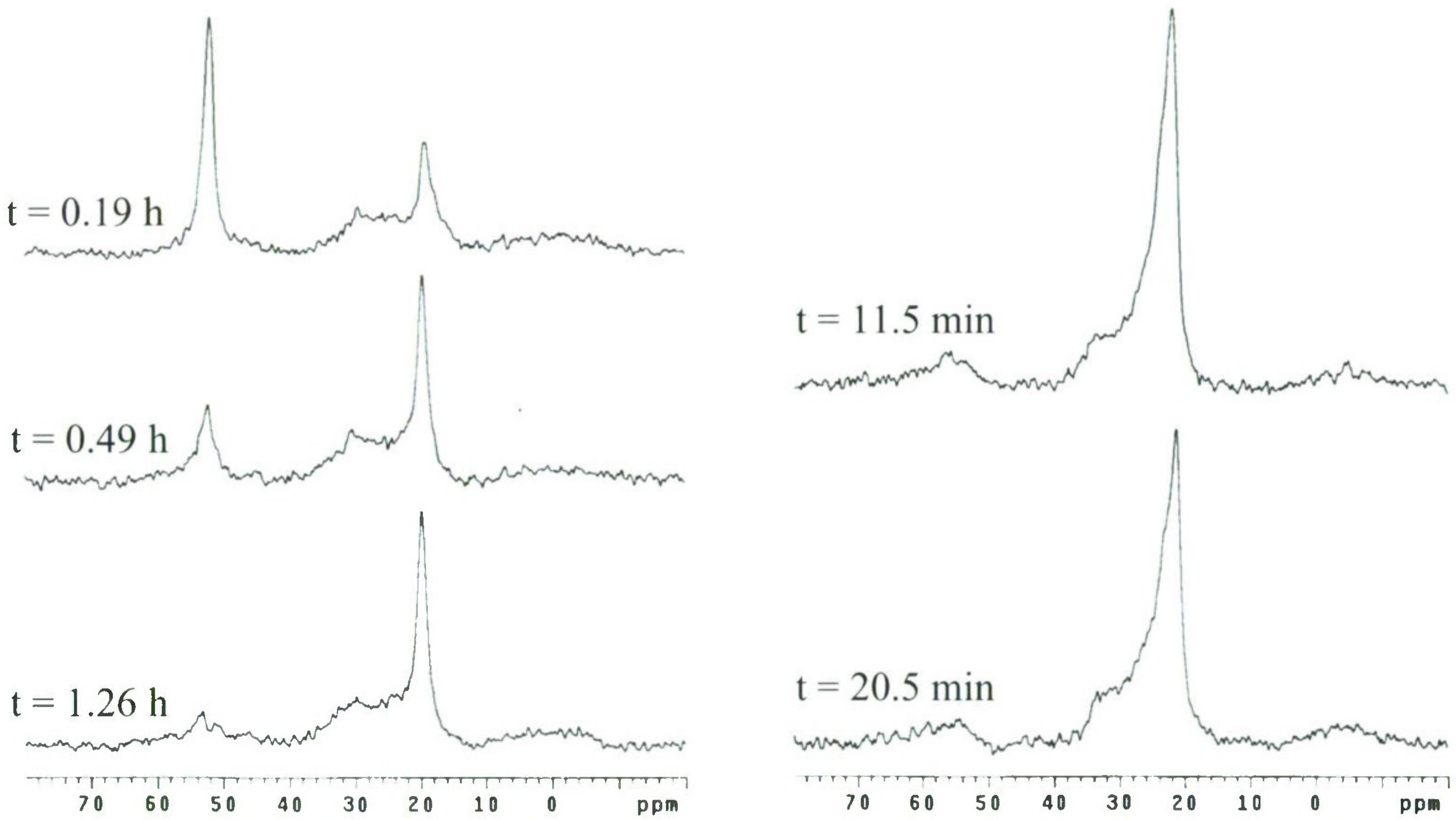

Figure B20. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.2035 g fresh (left) and 0.2564 g air-exposed (right) nTiO_2 #1, Run 1, at the indicated reaction times.

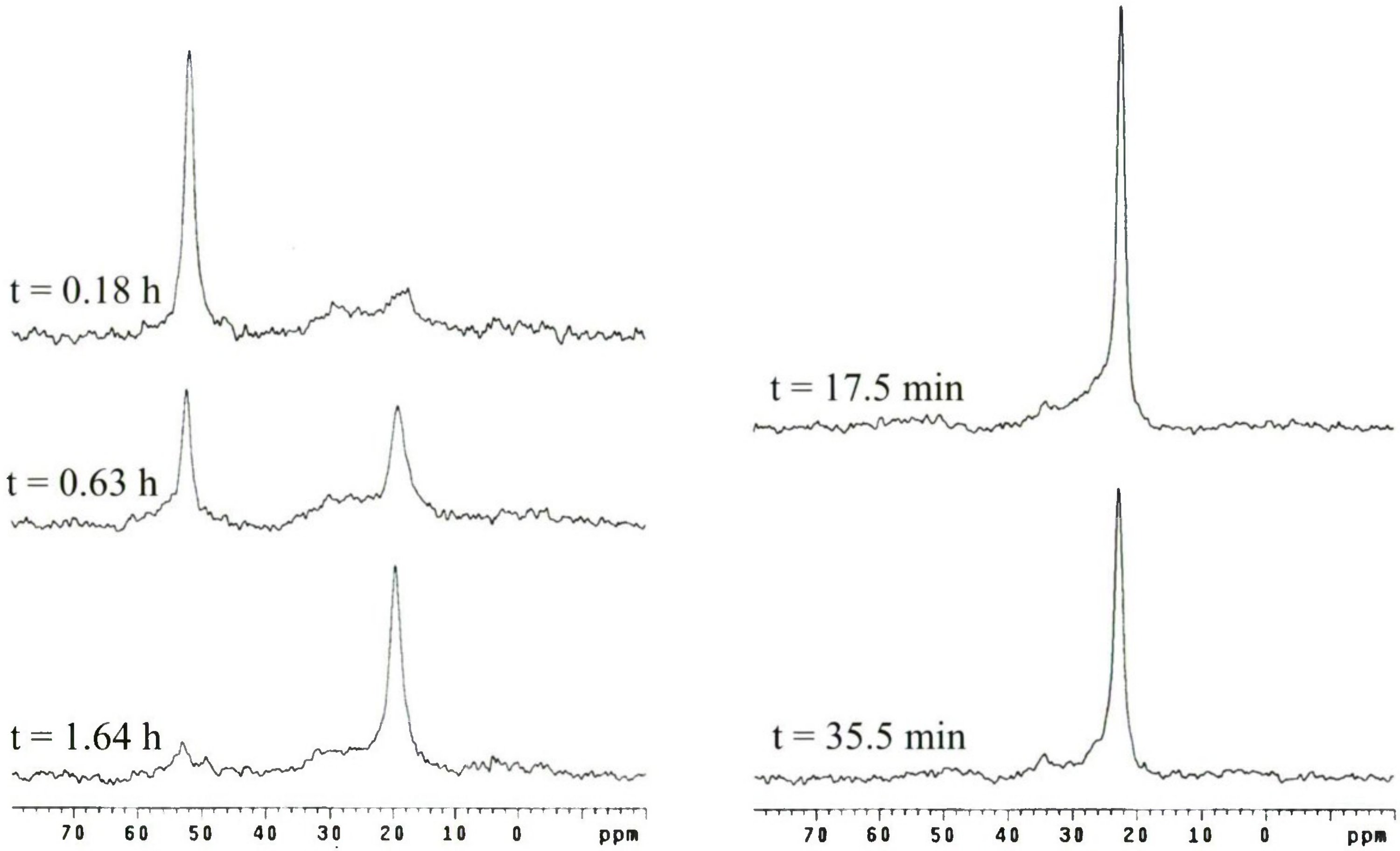

Figure B21. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.2061 g fresh (left) and 0.2550 g air-exposed (right) $nTiO_2$ #1, Run 2, at the indicated reaction times.

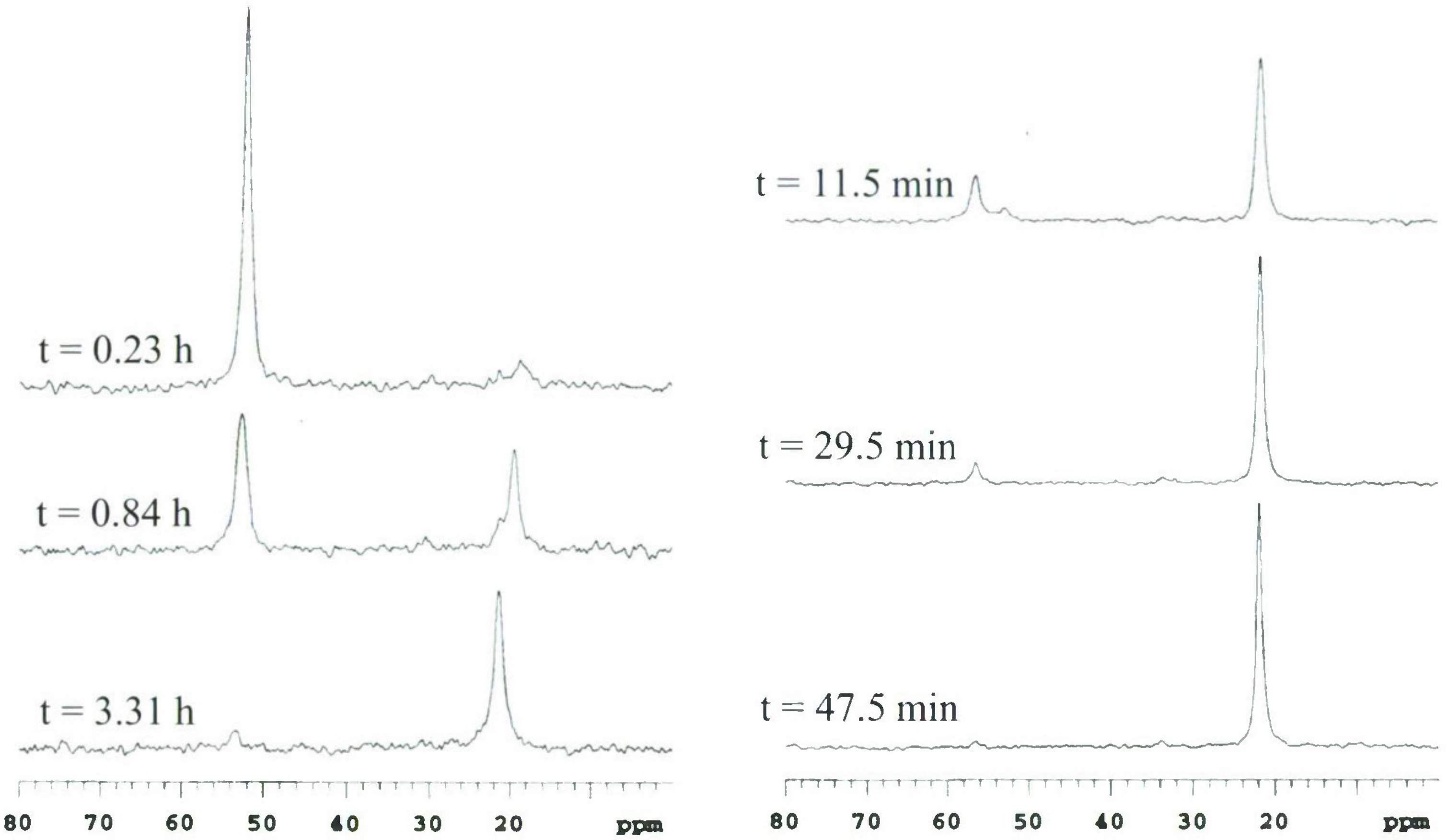

Figure B22. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.1321 g fresh (left) and 0.1619 g air-exposed (right) nTiO$_2$ #2 at the indicated reaction times.

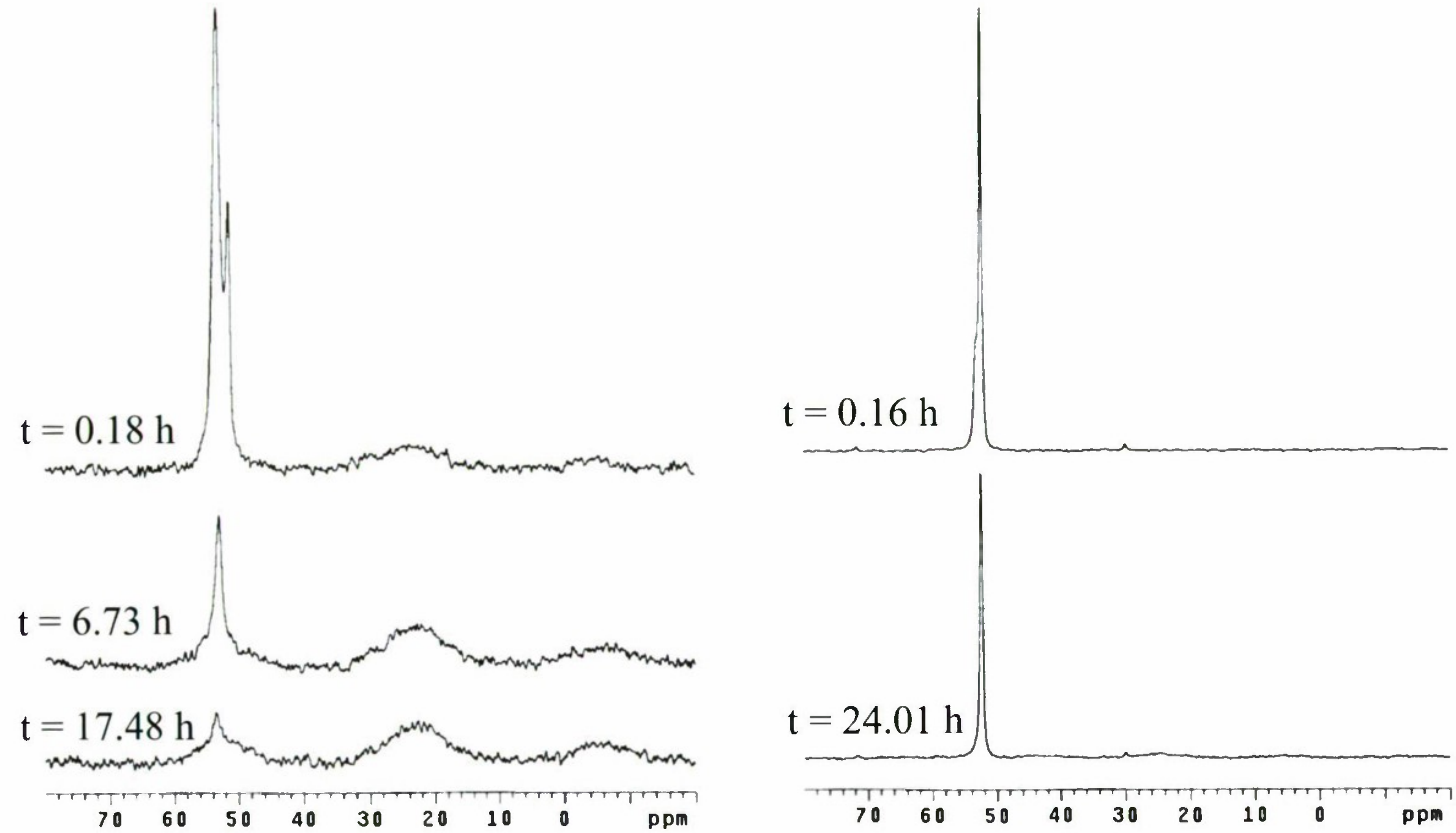

Figure B23. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.1456 g fresh (left) and 0.1890 g air-exposed (right) nMgO #1 at the indicated reaction times.

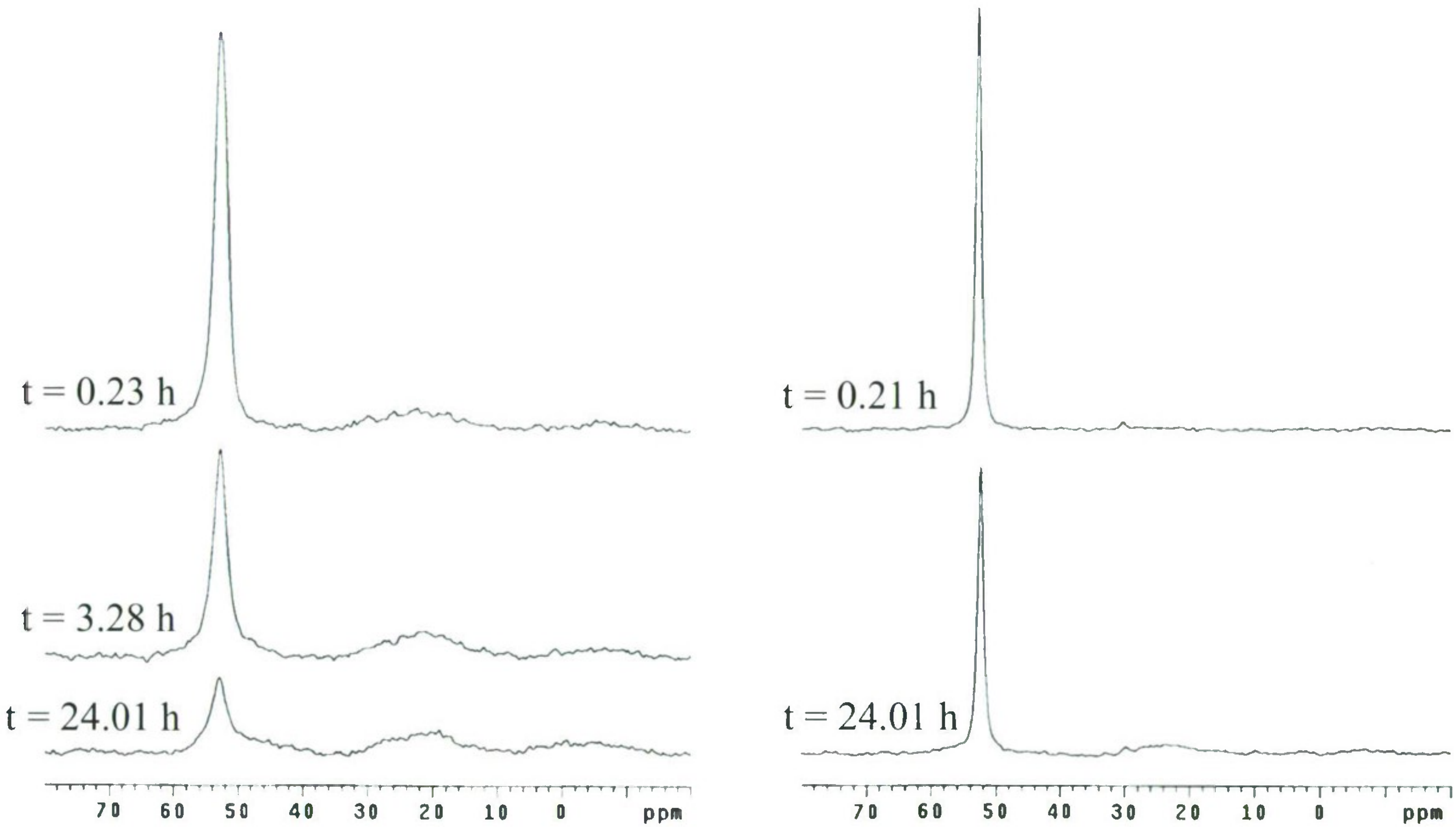

Figure B24. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.2146 g fresh (left) and 0.2475 g air-exposed (right) nMgO #2 at the indicated reaction times.

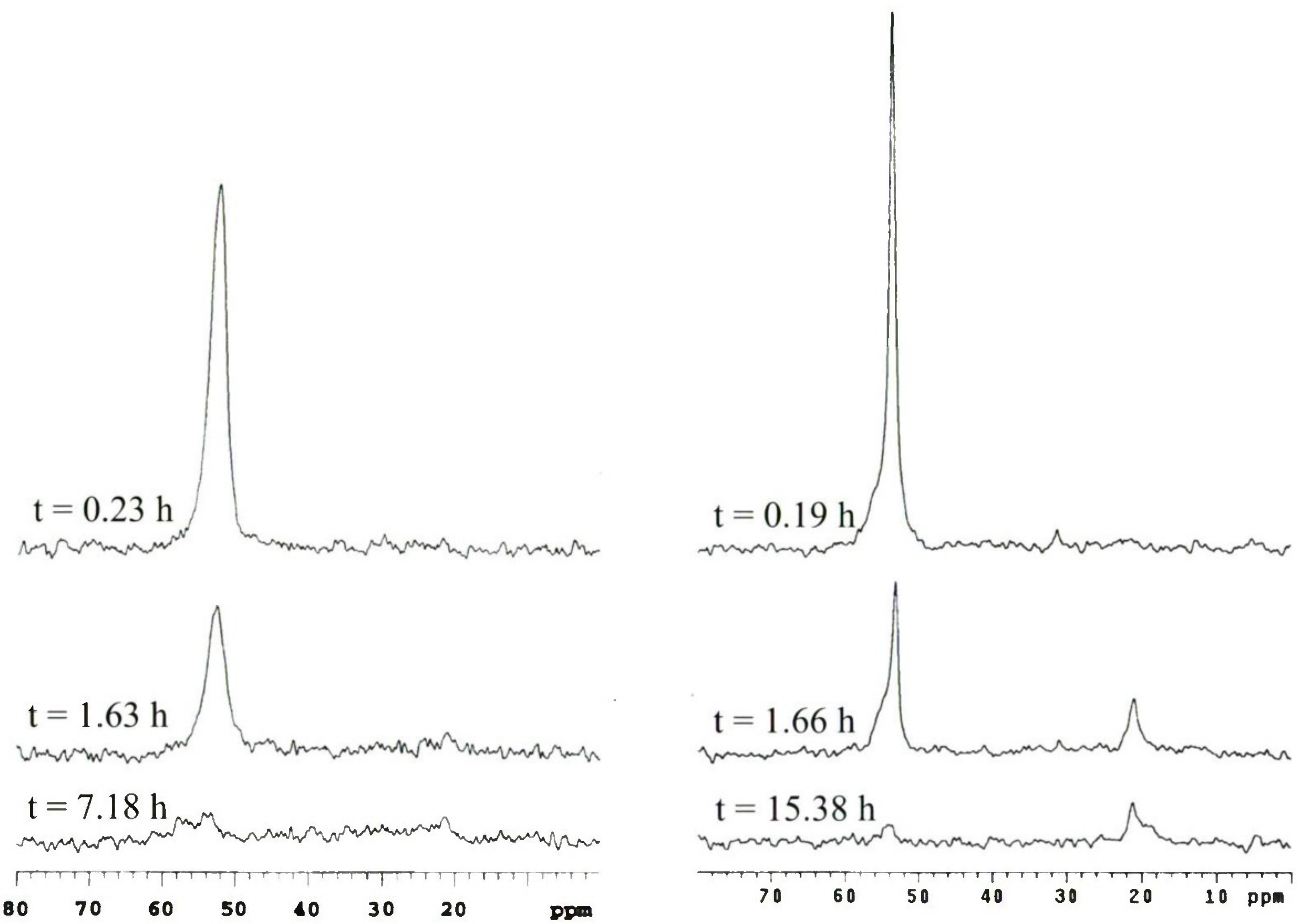

Figure B25. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.1969 g fresh (left) and 0.2294 g air-exposed (right) FAST-ACT at the indicated reaction times.

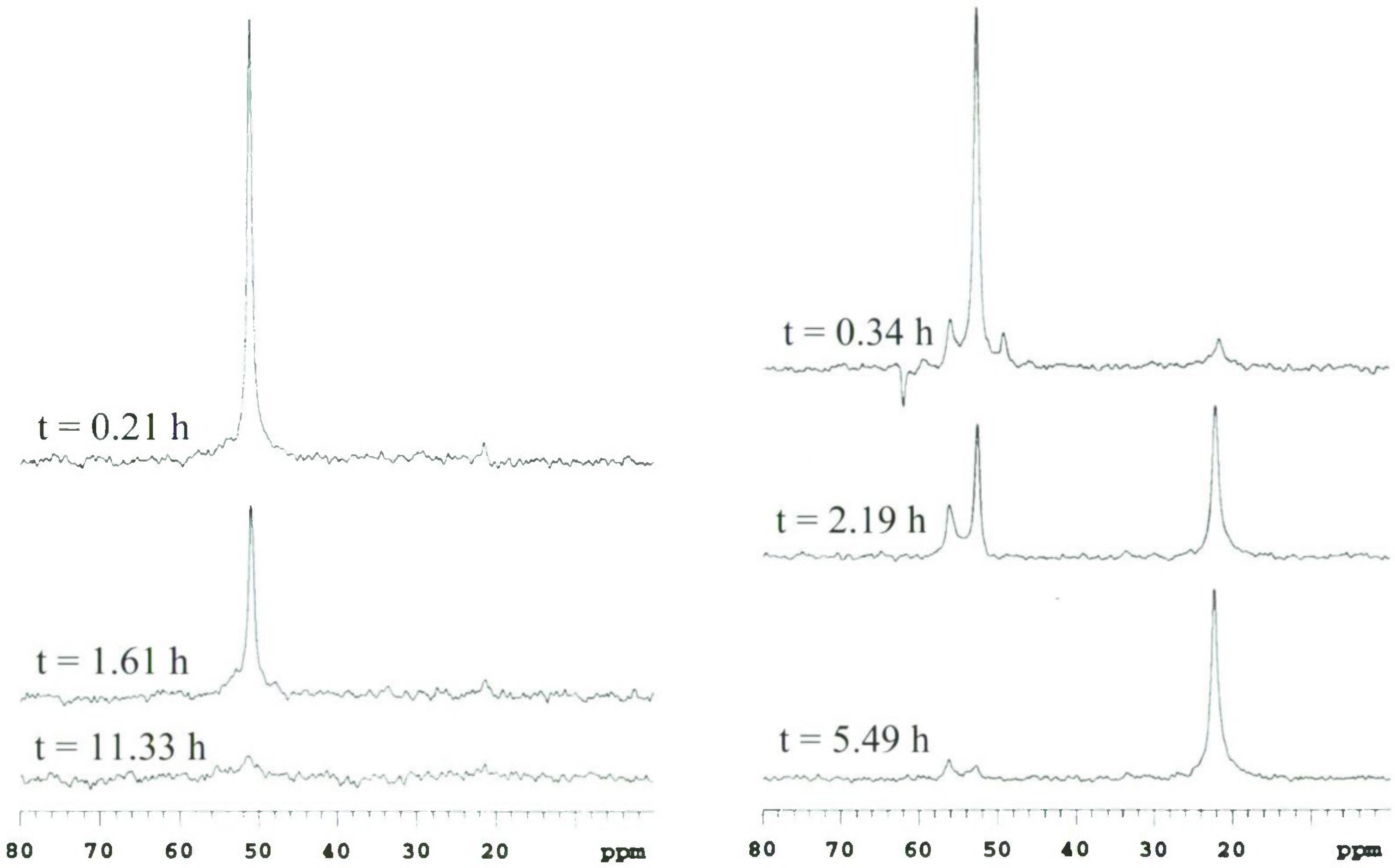

Figure B26. Select ^{31}P MAS NMR spectra obtained for 5 μL VX added to 0.1386 g fresh (left) and 0.1960 g air-exposed (right) FAST-ACT 2 at the indicated reaction times.

Blank

APPENDIX C
PANEL TEST DATA

PANEL TEST DATA

Table C1. Panel Test Data for the Decontamination of VX, GD, and HD on CARC Panels by Candidate Sorbents.

Sorbent	HD (16 μL added, six replicates)				GD (20 μL added, six replicates)			
	Contact (μL)	Residual (μL)	Total (μL)	% Decon	Contact (μL)	Residual (μL)	Total (μL)	% Decon
nMgO#1	1.8	2.4	4.2	74	1.9	0.92	2.8	86
	1.2	2.3	3.5	78	2.1	0.79	2.9	85
	1.8	2.4	4.2	74	1.0	1.1	2.1	89
	2.3	2.6	4.9	69	1.8	0.66	2.5	87
	2.3	2.6	4.9	69	1.0	1.3	2.3	88
	1.4	2.3	3.7	77	2.1	0.92	3.0	85
nMgO#2	2.4	2.3	4.7	69	1.4	1.1	2.5	87
	2.3	2.6	4.9	69	1.3	1.2	2.5	87
	2.8	2.7	5.5	63	1.7	1.3	3.0	85
	2.2	2.1	4.3	75	1.1	1.4	2.6	87
	2.5	2.3	4.8	69	2.4	0.92	3.5	82
	2.5	2.6	5.1	69	1.7	1.1	2.8	86
nTiO$_2$ #1	2.1	1.6	3.7	77	1.4	0.97	2.4	88
	2.9	1.9	4.8	70	1.4	1.1	2.5	87
	1.2	2.3	3.5	78	1.4	0.85	2.4	88
	1.9	–	–	–	1.4	1.5	2.9	85
	1.7	–	–	–	1.3	1.5	2.8	86
	2.1	–	–	–	1.6	1.2	2.8	86
nAl$_2$O$_3$	2.3	1.2	3.5	78	1.6	1.2	2.8	86
	2.3	1.4	3.7	77	1.2	1.2	2.4	88
	2.5	1.3	3.8	76	1.3	1.3	2.6	87
	3.1	1.6	4.7	71	0.8	1.6	2.4	88
	2.4	1.6	4.0	75	1.3	1.3	2.6	87
	2.5	1.4	3.9	76	1.1	1.5	2.6	87
A-200	2.0	1.6	3.6	78	1.8	0.71	2.5	87
	2.4	1.3	3.7	77	2.3	0.71	3.0	85
	2.5	1.8	4.3	73	1.8	0.53	2.3	88
	2.4	0.6	3.0	81	1.9	0.71	2.6	87
	3.3	0.9	4.2	74	1.9	0.71	2.6	87
	2.3	1.6	3.9	76	2.3	0.53	2.8	86
No Decon Control	14	1.0	15	94	10	1.1	11	55
	15	1.7	17	110	12	1.7	14	70
	12	2.0	14	88	11	1.9	13	65
	16	1.3	17	110	12	1.2	13	65
	13	1.7	15	94	12	2.3	14	70
	13	1.7	15	94	13	1.1	14	70