核磁共振冷冻测孔法及其在页岩纳米孔隙表征的应用

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摘要 页岩气已成为如今最具开采前景与价值的非常规天然气, 而以纳米级孔隙为主体的页岩孔隙结构极大地决定着其成藏机理与运移机制, 因此, 能否准确地表征页岩孔隙结构是影响页岩气资源评价合理与否的关键因素. 目前, 扫描电子显微镜、压汞法、氮气吸附法、CT法等已被大量用于页岩的孔隙特征研究, 然而由于页岩孔隙结构复杂、非均质性强等特点, 不同方法在表征时往往受到适用范围和测试精度等方面的限制. 针对新兴的核磁共振冷冻测孔法, 利用标准孔隙样品对该基于核磁共振原理的变温测孔技术进行了方法验证, 并将其用于页岩的孔隙度及孔径分布研究, 同时探讨了块状、磨碎两种样品形态对测试结果的影响. 测试结果表明该方法获取的孔隙度、孔径分布数据与压汞法、氮气吸附法在同一表征条件下吻合较好, 且样品磨碎后相较块状样品能一定程度地获取封闭的不连通孔隙信息. 该方法扰动小、直观、快速, 能够很好地获取2~1000 nm范围的孔隙结构信息, 可对其他测试手段进行补充和验证, 为页岩等低渗介质复杂孔隙结构表征研究提供了新方法. 研究除对技术特点与适用条件进行分析外, 也针对技术改进、应用拓展等方面提出了展望.

关键词 页岩气, 纳米孔隙, 微观结构, 核磁共振, 冷冻测孔法

随着勘探开发技术的突破与产量的快速增长, 页岩气已被公认为全球最具开采前景的非常规天然气. 研究表明, 其与常规天然气藏的差异主要源于储层特征及储气机理^[1,2], 常规储层的孔隙一般为毫米至微米级, 而页岩气储层的孔隙通常以纳米级孔隙为主体^[3,4], 两者的物理性质存在明显区别. 因此, 充分认识页岩微观孔隙结构, 不但是了解气体赋存状态、扩散-渗流过程的基础, 也是研究页岩气成藏机理以及油气勘探评价的关键^[5,6].

根据对相关文献的调研, 目前页岩孔隙结构的研究指标主要有孔隙率、孔径分布、孔比表面积、孔隙形态, 对其孔隙体系划分大多沿用国际理论与应用化学联合会(IUPAC)的划分方法, 将孔隙分为微孔

(<2 nm)、中孔(2~50 nm)、大孔(>50 nm). 此外, Maex等人^[7]还对多孔介质的表征方法进行了总结, 并将其归纳为三类(图1): 图像分析法(image analysis)、流体注入法(intrusive method)、非物质注入法(nonintrusive method). 其中, 图像分析法利用不同类型显微镜对多孔材料进行直接观察并获取图像, 常结合统计学方法获得部分定量信息; 流体注入法则在不同压力下将非润湿性流体或气体注入多孔介质获取体积变化曲线, 利用不同理论模型对结构进行表征, 目前较为常用的有压汞法、气体吸附法等; 非物质注入法主要有核磁共振法(nuclear magnetic resonance, NMR)、小角散射法(small-angle scattering, SAS)、微计算机断层扫描技术(micro-CT)等, 利用核磁共振、射线等物

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图1 孔隙结构测试方法对比图

Figure 1 Comparison of various measurement techniques of pore structures

理现象获取孔隙信息,在岩芯物性、结构研究方面展现出了一定优势。

基于非常规油气勘探的兴起,国内外学者利用不同方法开展了大量页岩孔隙的研究^[8,9],认为纳米级孔隙体系是控制烃类储藏能力和流体在裂缝网络中可迁移性的重要因素。Curtis等人^[10]利用双离子束系统(FIB-SEM)实现了样品切割和扫描的同时进行,提供的三维图像便于研究纳米孔隙的分布与连通性;田华等人^[11]将CO₂吸附、N₂吸附与压汞法联合使用,对泥页岩孔隙特征进行了全面研究。然而,由于页岩以纳米孔隙为主,具有结构复杂、连通性差、非均质性强等特点,使对其进行孔隙表征时,很多方法的适用性与可靠性受到了制约:图像分析法虽在研究孔隙形态方面具有优势,但其样品处理要求高,易形成“假孔隙”,受非均质性影响大,且图像分辨率会直接限制表征精度,通常用于定性分析,难以满足储层评价及开发的需求^[12~14];流体注入法获取的数据相对全面,但通常用于研究开孔体系,在样品预处理及实验过程中易导致微孔结构破坏^[15,16],常用的压汞法测量的是孔隙最大开口尺寸,而孔喉的存在往往会使结果偏离真实值,氮气吸附法测试耗时并难以用于大孔表征,且以上方法均难以覆盖页岩的孔隙分布范围,使得孔隙度等结果有所偏离,需多种方法补充与验证;非物质注入法通常具有快速、无损、简便

的特点,在页岩孔隙研究中发挥巨大作用,但部分方法测试价格昂贵,实验条件及测试范围有限^[17,18]。

核磁共振冷冻测孔法(nuclear magnetic resonance cryoporometry, NMR-C)作为一种新兴的间接表征技术,不但能覆盖纳米孔隙的测试范围,实现对同一样品的连续测量,还能直接、高效地获取孔径分布、孔隙度等信息,对样品扰动小,在页岩等低渗介质的纳米孔隙研究中展现出了极大的潜力,可对其他手段进行补充。该方法通过核磁共振信号记录变温条件下多孔介质孔隙内的相变过程,基于受限材料的相变理论,对多孔材料的孔隙度、孔径分布等性质进行深入研究^[19]。常规的核磁共振弛豫法不能反映孔隙的绝对孔径,需要进行系数换算得到孔径分布,存在一定误差,且对于孔径较小(小于10 nm)的样品测定信噪比较低,而NMR-C不但具有常规核磁共振技术的优势,还能提高微孔、中孔的测试精度,测试范围也能满足低渗页岩的需求。目前,国外已逐步将该方法应用于化学、生物、医学等领域^[20],并取得了丰富的研究成果,但国内还鲜见此方法的研究成果。Viel等人^[21]通过NMR-C探测了古代脱水的落叶松木材孔隙中的含水率;Gun'Ko等人^[22]利用高分辨率核磁观察了健康的及骨质疏松的人类骨骼,利用NMR-C法发现后者骨骼中含有更多2 nm以上的孔隙;Korb^[23]利用NMR-C法对不同水灰比的水泥试样进行了测试,

认为该方法在2~500 nm测试范围内有良好的精度及可重复性。可见, NMR-C是一种极具研究意义与应用价值的孔隙结构表征方法。目前, 该方法在岩石空隙表征, 特别是页岩孔隙研究方面的应用鲜有报道, Firouzi等人^[24]曾做过尝试, 但由于实验设备受限并未获得完整的页岩孔径分布数据。此外, 页岩中有相当一部分孔隙是互不连通的, 而不连通空隙中赋存的气经过压裂改造是可供开采的, 因此考虑样品形态对测试结果的影响极具实际意义, 但目前缺乏块状样品及磨碎样品间孔隙结构分析的对比研究^[25]。本研究利用不同孔径的标准材料对核磁共振冷冻测孔法的测试精度进行验证, 并尝试采用该方法表征块体和磨碎页岩样品的孔隙结构, 将实验结果与压汞法、气体吸附法比对, 对其适用性与可靠性进行讨论, 为页岩等微孔、中孔较多的纳米孔隙介质研究提供借鉴。

1 基本原理与方法

核磁共振是磁矩不为零的原子核在外磁场作用下自旋能级发生塞曼分裂, 共振吸收某一定频率射频辐射的物理过程^[26], 而停止射频照射后原子核从激化状态回复到平衡状态的过程称为弛豫^[27,28], 核磁共振冷冻测孔法的实质是利用流体固、液态核磁共振弛豫性质的差异来表征孔隙结构特征。在实际测量过程中, 首先将某种液体(一般为润湿性液体)饱和和填充于待测的多孔固体材料中, 通过仪器配备的冷却装置进行变温操作, 测量相应相变过程的液体变化量, 从而获得熔化(或凝固)曲线, 分析孔隙的相关信息。该方法是由Strange等人^[29]基于Gibbs-Thomson方程提出的一种定量测孔方法, Hansen等人^[30]对其进行了补充与发展。

若假定尺寸为 x 的孔隙体积为 $V(x)$, 孔内晶体的熔点为 $T_m(x)$, 则孔体积分布如下:

$$\frac{dV}{dx} = \frac{dV}{dT_m(x)} \times \frac{dT_m(x)}{dx}. \quad (1)$$

根据Gibbs-Thomson方程

$$\Delta T_m(x) = T_m^\infty - T_m(x) = -\frac{4\sigma_{sl}T_m^\infty}{x\Delta H_f\rho_s}\cos(\phi), \quad (2)$$

式中, T_m^∞ 为固体熔点; σ_{sl} 为固-液界面的表面能; ΔH_f 为宏观物质的熔化焓(每克物质); ρ_s 为固体密度; ϕ 为液体与孔壁的接触角。式(2)还可简化表达为^[31]

$$\Delta T_m(x) = \frac{k_g \cdot k_s \cdot k_i}{x} = \frac{k_{GT}}{x}, \quad (3)$$

式中, k_g 为几何常量; $k_s = \frac{T_m^\infty}{\Delta H_f\rho_s}$, 为与固-液体系相关的常量; k_i 则是与界面能相关的项。三者可统一用常量 k_{GT} 表示。根据式(1)和(3), 可得如下:

$$\frac{dV}{dx} = \frac{k_{GT}}{x^2} \times \frac{dV}{dT_m(x)}. \quad (4)$$

通常认为核磁信号强度 I 与孔体积 V 成正比关系, 则

$$\frac{dV}{dx} \propto \frac{dI}{dx} = \frac{k_{GT}}{x^2} \times \frac{dI}{dT_m(x)}. \quad (5)$$

实验过程中, 我们可以获得 I 与温度 T 的对应曲线, 只需确定比例常数 k_{GT} , 将温度转换成孔径, 即可求得样品的孔径分布^[32], 孔隙度则是将总的核磁信号强度转化成孔隙体积从而获得。

2 标准孔隙材料实验验证

为测试核磁共振冷冻测孔法的可靠性及适用性, 利用其对已知孔径的标准样品进行孔径表征。本研究选用了孔径范围为7~9 nm的SBA-15分子筛以及孔径为24 nm的可控纳米多孔玻璃(controlled pore glass, CPG)作为测试样品。SBA-15是以嵌段共聚物为模板剂, 在酸性条件下合成的具有二维六方通孔结构的介孔硅基分子筛, 其透射电子显微镜(transmission electron microscope, TEM)图像如图2所示, 样品为粉末状, 孔径范围为7~9 nm, 粒度为1~2 μm , BET比表面积为550~600 m^2/g ; CPG为二氧化硅材质的微孔玻璃小球, 孔径均匀、孔道连通, 可通过控制分相温度、分相时间等参数调控其孔径尺寸, 本文采用的

图2 SBA-15分子筛透射电子显微镜图像

Figure 2 Transmission Electron Microscope (TEM) images of SBA-15 molecular sieve

CPG材料孔径为24 nm.

两种样品皆在真空强制饱水后,于核磁共振孔隙分析仪中进行变温操作,变温范围从 $-24\sim 0^{\circ}\text{C}$,温度波动为 $\pm 0.02^{\circ}\text{C}$,最小温度梯度为 0.1°C ,利用Carr-Purcell-Meiboom-Gill(CPMG)序列进行核磁信号采集.实验结果如图3所示,SBA-15样品孔隙主要分布于6~10 nm,其中峰点孔径为7.9 nm;24 nm的CPG样品孔隙主要分布于15~35 nm,其中峰点孔径为24.6 nm,测试结果皆与已知参数吻合较好.

综上可知,核磁共振冷冻测孔法对于不同孔径范围的材料具有较强的表征能力以及较高的表征精度.国外部分学者也进行过类似实验,根据对多种尺寸的硅胶^[33]、MCM-41分子筛^[34,35]等材料进行不同方法间的结果比对,认为NMR-C法对于纳米材料的研究具有一定优势,可对其他方法进行补充.因此,该方法可进一步应用于非规则样品的孔隙分析,本研究尝试将其用于表征低渗页岩的孔隙结构.

3 页岩纳米孔隙结构测试分析

3.1 测试材料及方法

研究选取我国第一口页岩气井——四川威远威201井深度约为2700 m的页岩作为样品,分别制成块状、磨碎(40~60目)两类样品,利用核磁共振冷冻测孔法、压汞法与氮气吸附法对其孔隙结构进行表征.其中,核磁共振冷冻测孔法采用Niumag NMRC12-010V-T型仪器,块状、磨碎样品分别烘干、称重并进行真空饱和,抽气6 h,常压下静置8 h,变温操作范围为 $-36\sim 7^{\circ}\text{C}$,温度波动为 $\pm 0.02^{\circ}\text{C}$,最小温度梯度为

0.1°C ,利用CPMG序列进行核磁信号采集;压汞法测试块状样品,采用9500型压汞仪,最大进汞压力为413.7 MPa,接触角为 130° ,孔径测试范围为3 nm~500 μm ;氮气吸附法测试磨碎样品,采用3H-2000PS2型仪器,测试前先在 200°C 高温下真空脱气6 h,然后在恒温浴温度77.3 K条件下进行低温吸附.

3.2 测试结果分析

(i) 核磁共振冷冻法测试结果.核磁共振冷冻测孔法需先对样品进行饱和,因此饱和液体的选择十分重要.通常采用不易挥发,不与样品发生反应,相变前后核磁信号差异明显,以及润湿性较好能通过毛细作用自发进入小孔的液体.且由式(3)可知,液体 k_{GT} 越大,相同孔径引起的温度变化就越大,仪器分辨率就越高,因此在其他条件满足的前提下,应尽量选择 k_{GT} 较大的液体.目前,冷冻测孔法可用的饱和液体主要有水、环己烷等.水对于页岩样品,可能会与其中的黏土矿物颗粒等发生物理、化学反应从而会影响测试结果,故需和其他方法测试结果进行比对,对该影响进行评定.环己烷为无色有刺激性气味的液体,不溶于水,溶于多数有机溶剂,其分子式为 C_6H_{12} ,研究表明,水的 k_{GT} 约为58.2 K nm,环己烷的 k_{GT} 为108~179 K nm^[36],故环己烷的精度更高且测试范围更广,但环己烷分子相比水分子较大,难以充分进入小孔,特别是连通性较差的页岩样品,故水对微孔的表征要优于环己烷.综上,本研究选用水作为块状样品的饱和溶剂,选用水、环己烷作为磨碎样品的饱和溶剂,将两者结果进行对比分析.结果表明,NMR-C法测得块状样品的孔隙度约为3.2%,磨碎样

图3 SBA-15分子筛NMR-C法(a)和CPG材料NMR-C法(b)的孔径分布结果

Figure 3 Pore size distributions of SBA-15 (a) and CPG (b) using NMR-C

品的孔隙度约为5.7%，前者孔径分布相对均匀，后者孔径分布主要集中于大孔处。如图4所示，针对磨碎样品采用两种饱和和液体饱和的测试结果较为相近，孔隙分布的峰值位于100~200 nm处，相关研究也曾证实，威201井处页岩孔隙大小介于10~900 nm，主要为150 nm左右^[37]。对于孔径小于10 nm的孔隙，由于环己烷分子较大未能很好地进入小孔中，其表征效果与水相比较差。而水与页岩中黏土矿物颗粒间的水化学反应对测试结果影响不大，可见页岩在-30~0℃低温环境下的水岩反应极不活跃，因此并不会对页岩孔隙产生显著的破坏性影响。

(ii) 不同方法结果对比。对于块状样品，其主要反映连通空隙的结构特征，如图5所示，NMR-C法与压汞法测试结果极为相近，其中前者的孔隙度为3.2%，后者孔隙度为3.7%，样品孔径分布范围较广且均匀，而NMR-C法对于微孔的刻画更为精细。对于磨碎样品，页岩的孔隙以中孔、大孔为主，呈现多峰形态，其中100~200和15~30 nm范围内孔隙较多，孔隙度约为5.7%，NMR-C法与氮气吸附法在同一区段孔径分布趋势大体一致，对峰值的刻画吻合程度较高。氮气吸附法根据不同试验压力下的氮气吸附量，绘制吸附和脱附等温线，理论上本方法所能测定的最小孔径为探针气体的分子直径，最大孔径由高相对压力下测定探针气体吸附量的实际难度决定，其可测量孔半径下限在0.3 nm左右，可测最大孔半径范围为50~75 nm^[38]，而NMR-C法则能较完整地获取纳米尺度的孔隙信息，是对其他方法很好的补充与验证。

根据不同形态样品的累计孔体积分布曲线可知(图6)，磨碎样品孔隙体积普遍高于块状样品，且在

图4 页岩磨碎样品核磁共振冷冻测孔法孔径分布图
Figure 4 Pore size distributions of pulverized shale samples by NMR-C

图5 NMR-C与压汞法、氮气吸附法孔径分布结果对比图
Figure 5 The comparison of NMR-C, MICP and NAD on pore size distributions

图6 不同形态样品累计孔体积分布曲线图
Figure 6 Cumulative pore volume distribution curves of the bulk and pulverized shale samples by NMR-C

中、大孔区段表现明显，推测其原因为碎样处理后使得部分封闭的非连通孔隙被打开，也说明测试样品中含有较多的封闭孔隙。磨碎样品的测试使得空隙表征更加完全，测试结果与介质的总孔隙度更为接近。因此，核磁共振冷冻测孔法也可进一步用于有效孔隙度、总孔隙度的表征探讨，这对页岩气开采评价极具实际价值。

综上，核磁共振冷冻测孔法作为一种扰动小、快速的孔隙表征方法，不但具有较高精度，且能完全覆盖纳米孔隙分布范围，在纳米介质孔隙研究方面具有一定优势，是对其他方法的验证与补充，将在低渗介质的相关研究中展现出巨大潜力。

4 结论与展望

目前，NMR-C已被广泛用于研究介孔二氧化硅、生物细胞、木材等材料，而本研究表明，其在页岩等

岩石的孔隙表征方面也具有广阔的应用前景. 相较于传统的方法, NMR-C在纳米介质孔隙研究方面的优点可概括如下: (1) 该方法较压汞法、氮气吸附法等能较好地表征2~1000 nm范围内的孔隙结构, 且可在水相环境下进行测试; (2) NMR-C利用核磁共振技术对孔内信息进行直接获取, 减小了对孔隙结构的破坏, 也使得测试过程更加直接、快速; (3) 通过改变样品形态以及利用流体的毛细、扩散等作用, NMR-C可获得闭孔信息, 可用于低渗介质有效孔隙度、总孔隙度的对比研究.

同时, 部分学者通过理论分析认为, 利用不同变温方式获得的熔化、凝固过程的温度变化 ΔT_m 和 ΔT_f , 其比值 $\Delta T_m/\Delta T_f$ 与空隙的几何形状(比表面积)相关, 球状、圆柱状、狭缝状空隙的 $\Delta T_m/\Delta T_f$ 比值分别约为2/3, 1/2和0, 且相关结论已得到了部分实验的证实^[39], 若能继续深入研究熔化-凝固曲线特征, 建立几何形态评价方法, 则可加深对复杂介质空隙形态的认识.

当然, 该方法本身也存在一定限制: (1) 由于页岩孔隙的孔隙度、孔径通常比常规储层小, 且可能含有顺磁性物质, 使得NMR实验结果的信噪比低, 弛豫时间短, 会一定程度地影响测试精度; (2) 核磁共振冷冻测孔法实验参数的选取会直接影响分析结果的可靠性, 如回波时间、液体选取、参数设定等, 需要更深入的研究来确定合理的实验参数; (3) 纳米孔隙会对流体的热力学性质产生不容忽视的尺度效应, 特别是对于孔径小于10 nm的材料, 因此需对Gibbs-Thomson方程等理论模型进行改进与补充.

综上所述, 核磁共振冷冻测孔法极大地丰富了孔隙结构的表征方法, 可作为其他方法的补充与校正, 且在页岩等岩石介质研究领域具有较强的应用价值. 若能将NMR-C与其他核磁技术相结合(如核磁共振光谱法、核磁共振成像技术等), 则可深入研究孔隙的非均一性、连通性、交界面相互作用等特性, 得到更全面、综合的孔隙结构分析结果, 值得进一步的研究与推广.

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Nuclear magnetic resonance cryoporometry as a tool to measure pore size distribution of shale rock

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Shale gas has recently emerged as an energy source that offers the opportunity for a number of countries for national energy independence and security. Shale gas is also less-carbon energy compared to coal and oil which can immediately serve as a blue bridge from carbon-intensive energy to renewables. In order to optimize the shale well productivity, characterization and quantification of shale pore architecture is one of the key parameters to model the gas flow behavior in subsurface shales. Transport properties, adsorption and diffusion, of shale gas are influenced, and sometimes even dominated by the pore structure of shales including the size, shape and connectivity of pore and pore networks. To accurately characterize the pore structure of shale is a challenging task in geoscience community. Various techniques, such as Scanning Electron Microscope (SEM), Mercury Intrusion Porosimetry (MIP) and Nitrogen Adsorption Method (NAM) and others, have been widely used to characterize pore structure of geomaterials. However, the built-in limitations of each technique were commonly reported in terms of applicability and accuracy due to the complexity and heterogeneity of the shale pore structure. Taking NAM and MIP for instance, these two techniques routinely involve material alteration which makes them potentially sensitive to contraction and pore interconnectivity, as well as the pressure-induced damage. The nuclear magnetic resonance cryoporometry, a novel and emerging technique, can probe pore size distributions from nano- to micro-scales based upon the depressed melting point of a confined liquid. Liquid and solid states in the NMR cryoporometry differ greatly in the transverse relaxation time, generally more than three orders of magnitude, which provides a relatively wide range for measuring pore size distribution. The resolution in NMR cryoporometry, are controlled by the Gibbs-Thomson coefficient of the liquid imbibed in a sample as well as the instrumental parameters such as temperature spread in the sample and temperature step size. In this study, two standard molecular sieves with pre-known pore structures were initially used to assess the applicability and the accuracy of this technique. Additionally, in order to evaluate the NMR cryoporometry results, both MIP and NAM were employed to characterize the pore structure on the same sample. We tested on both bulk matrix specimens and pulverized shale samples. The results demonstrate that MIP and NAM were comparable NMR cryoporometry and the pore size distributions were found to be similar across these techniques on both bulk and pulverized samples. The NMR cryoporometry was found to be a promising technique to analyze both total and effective porosities by measuring the same rock with pulverized and bulk sample, respectively. Besides pore size distribution and porosity, NMR cryoporometry has a unique feature to analyze larger and potentially arbitrarily-shaped objects and is applicable to samples in aqueous environment. Although it has not been widely used as a stand-alone technique, NMR cryoporometry has become a favored tool for calibrating NMR relaxometry due to its ability to provide accurate, reproducible, and unambiguous results. NMR cryoporometry is a promising and powerful tool when combined with other techniques including NMR relaxometry, spectroscopy, diffusion, and imaging. To summarize, NMR cryoporometry shows the applicability of pore characterization for porous absorbents and absorbates and it provides a wider spectrum of pore information including pore morphology, connectivity, heterogeneity, fluid-surface interactions, and the behavior of binary liquids. It is a promising and valuable technique for pore structure characterization for gas shales. In addition, it will help us improve the understanding of pore surface interactions and its related phenomena, and to discover the fundamental mechanisms behind the behavior of molecules in the confinement when combining with powerful computer modeling simulations.

shale gas, nanopore, microstructure, nuclear magnetic resonance, cryoporometry

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